CHEMISTRY

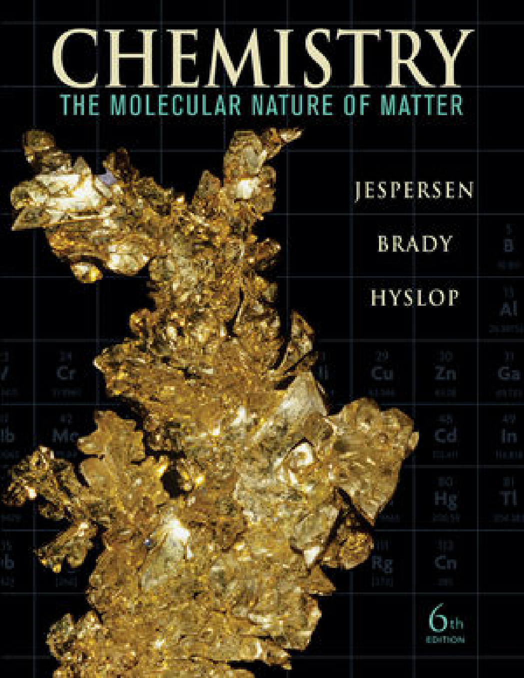
THE MOLECULAR NATURE OF MATTER

JESPERSEN

BRADY

HYSLOP

6th EDITION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Sixth Edition

Chemistry

The Molecular Nature of Matter

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Sixth Edition

Chemistry

The Molecular Nature of Matter

Neil D. Jespersen
St. John's University, New York

James E. Brady
St. John's University, New York

In collaboration with **Alison Hyslop**
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About the Authors

Neil D. Jespersen is a Professor of Chemistry at St. John's University in New York. He earned a B.S. with Special Attainments in Chemistry at Washington and Lee University (VA) and his Ph.D. in Analytical Chemistry with Joseph Jordan at The Pennsylvania State University. He has received awards for excellence in teaching and research from St. John's University and the E. Emmit Reid Award in college teaching from the American Chemical Society's Middle Atlantic Region. He chaired the Department of Chemistry for 6 years and has mentored the St. John's student ACS club for over 30 years while continuing to enjoy teaching Quantitative and Instrumental Analysis courses, along with General Chemistry. He has been an active contributor to the Eastern Analytical Symposium, chairing it in 1991. Neil has authored the Barrons AP Chemistry Study Guide; has edited 2 books on Instrumental Analysis and Thermal Analysis; and has 4 chapters in research monographs, 50 refereed publications, and 150 abstracts and presentations.

He is active at the local, regional and national levels of the American Chemical Society, and was recently elected to the ACS Board of Directors. When there is free time you can find him playing tennis, baseball with four grandchildren, or traveling with his wife Marilyn.

James E. Brady received his BA degree from Hofstra College in 1959 and his Ph.D. from Penn State University under the direction of C. David Schmulbach in 1963. He is Professor Emeritus at St. John's University, New York, where he taught graduate and undergraduate courses for 35 years. His first textbook, *General Chemistry: Principles and Structure*, coauthored with Gerard Humiston, was published in 1975. An innovative feature of the text was 3D illustrations of molecules and crystal structures that could be studied with a stereo viewer that came tucked into a pocket inside the rear cover of the book. The popularity of his approach to teaching general chemistry is evident in the way his books have shaped the evolution of textbooks over the last 35 years. His useful *chemical tools* approach toward teaching problem solving was introduced by him at the 12th Biennial Conference on Chemical Education at UC Davis in 1992 and continues to evolve. He has been the principal coauthor of various versions of this text, along with John Holum, Joel Russell, Fred Senese, and Neil Jespersen. He is particularly pleased to be a member of the current author team.

In 1999, Jim retired from St. John's University to devote more time to writing, and since then he has coauthored three editions of this text. He and his wife, June, enjoy their current home in Jacksonville, Florida. Jim is an avid photographer and many of his photos of surfers have been published in the local newspaper.

Alison Hyslop received her BA degree from Macalester College in 1986 and her Ph.D. from the University of Pennsylvania under the direction of Michael J. Therien in 1998. She is an Associate Professor at St. John's University, New York, where she has been teaching graduate and undergraduate courses since 2000. She was a visiting Assistant Professor at Trinity College (CT) from 1998 to 1999. She was a visiting scholar at Columbia University (NY) in 2005 and in 2007 and at Brooklyn College in 2009, where she worked on research projects in the laboratory of Brian Gibney. Her research focuses on the synthesis and study of porphyrin-based light harvesting compounds.

When not in the laboratory, she likes to hike in upstate New York, and practice tae kwon do.

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Preface

This textbook represents a significant revision of the fifth edition of *Chemistry: Matter and Its Changes* by James E. Brady, Frederick Senese, and Neil D. Jespersen. A new title was chosen to more closely reflect the increased emphasis that we have placed on the intimate relationship that exists between structure at the submicroscopic molecular level and the observable macroscopic properties of matter.

In this edition, it is our pleasure to have **Neil Jespersen** take on the role of lead author. Neil is a respected educator and an award-winning teacher who has more than proven himself in his role as a contributing author on the previous edition. We are fortunate to have him take the helm, and we are confident in his ability to carry the text forward into future editions. It is also our pleasure to welcome **Alison Hyslop** to the author team. Alison is an inorganic chemist with more than 10 years of experience teaching graduate and undergraduate inorganic chemistry as well as general chemistry. She brings to the team a commitment to excellence in teaching and an understanding of issues that stand in the way of student learning. We are excited about her contributions to this new edition.

Philosophy and Goals

The philosophy of the text is based on our conviction that a general chemistry course serves a variety of goals in the education of a student. First, of course, it must provide a sound foundation in the basic facts and concepts of chemistry upon which theoretical models can be constructed. The general chemistry course should also give the student an appreciation of the central role that chemistry plays among the sciences, as well as the importance of chemistry in society and day-to-day living. In addition, it should enable the student to develop skills in analytical thinking and problem solving. With these thoughts in mind, our aim in structuring the text was to provide a logical progression of topics arranged to provide the maximum flexibility for the teacher in organizing his or her course.

In revising this text, we were **guided by three principal goals**. The **first** was to strengthen the connection between observations on the macroscopic scale and the behavior of atoms, molecules, and ions at the atomic level. The **second** was to further enhance our already robust approach to teaching problem-solving skills. The **third** goal was to provide a seamless, total solution to the General Chemistry course by fully integrating the textbook content with the online assessment and resources delivered within ***WileyPLUS.***

Emphasizing the Molecular View of Matter

The value of the molecular approach in teaching chemistry is well accepted and has always been a cornerstone in the approach taken by Professor Brady and his co-authors in presenting chemistry to students. From his first text, in which novel three-dimensional computer-drawn representations of molecules and crystal structures were presented and observed using stereoscopic viewers, up through the 5th edition of this text, the atomic/molecular view has dominated the pedagogy. This new edition builds on that tradition by employing the "molecular basis of chemistry" as a powerful central theme of the text. Through this approach, the student will gain a sound appreciation of the nature of matter and how structure determines properties. Some actions we have taken to accomplish this are as follows:

- **Chapter One: Chemistry and the Atomic/Molecular View of Matter** The new edition begins with a new chapter (chapter one) that sets the tone for the entire book. It lays the groundwork for the atomic and molecular view of matter and outlines how these concepts are used throughout the text. Included is a discussion of what chemistry is and the kinds of activities that chemists participate in. We provide a brief introduction to atomic structure and introduce students to the way we visualize molecules and chemical reactions.

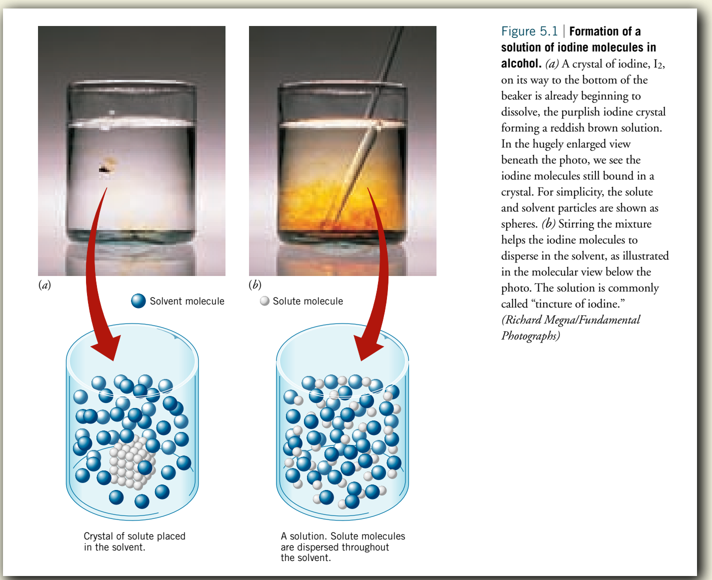

(a)
(b)
Solvent molecule
Solute molecule
Crystal of solute placed in the solvent.
A solution. Solute molecules are dispersed throughout the solvent.

Figure 5.1 | **Formation of a solution of iodine molecules in alcohol.** *(a)* A crystal of iodine, I_2, on its way to the bottom of the beaker is already beginning to dissolve, the purplish iodine crystal forming a reddish brown solution. In the hugely enlarged view beneath the photo, we see the iodine molecules still bound in a crystal. For simplicity, the solute and solvent particles are shown as spheres. *(b)* Stirring the mixture helps the iodine molecules to disperse in the solvent, as illustrated in the molecular view below the photo. The solution is commonly called "tincture of iodine." *(Richard Megna/Fundamental Photographs)*

- **Macro-to-Micro Illustrations** To help students make the connection between the macroscopic world we see and events that take place at the molecular level, we have a substantial number of illustrations that combine both views. A photograph, for example, will show a chemical reaction as well as an artist's rendition of the chemical interpretation of what is taking place between the atoms, molecules, or ions involved. We have also increased the number of illustrations that visualize reactions at the molecular level. The goal is to show how models of nature enable chemists to better understand their observations and to get students to visualize events at the molecular level.

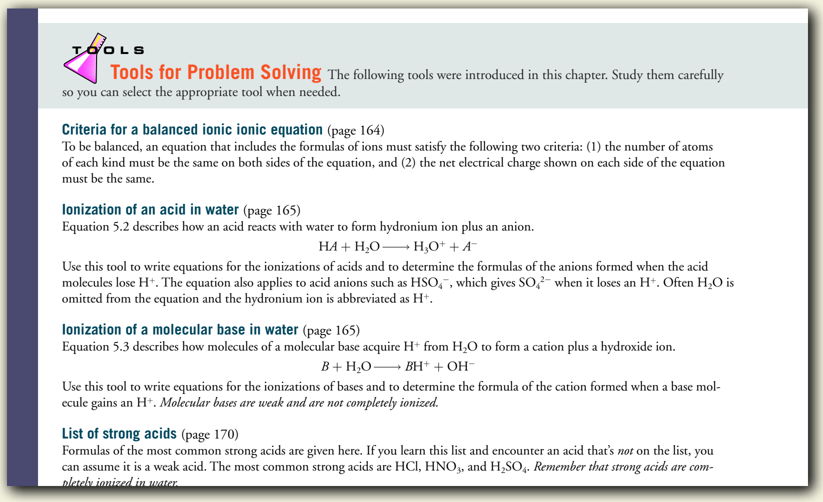
- **Molecular Interpretations** Significant use is made of molecular interpretations, and substantial rewriting of the chapter material has taken place. Where required, new figures have been drawn to provide visual meaning to accompanying discussions.

- **New Visual Exercises** In the end-of-chapter Questions and Problems, we include exercises that have a visual component requiring students to apply molecular concepts developed in the chapter discussions.

Developing Problem-solving Skills

We strongly believe that problem solving reinforces the learning of concepts and that assisting students in improving their skills in this area is one of the critical aspects of teaching chemistry. We also believe that it is possible to accommodate students who come into the course with a wide range of problem-solving skills. This is reflected in the attention paid to problem solving in the 6th Edition. In this new edition we have expanded and further refined the tools that students have available to develop their ability to analyze and solve problems.

- We continue to use a **"chemical tools"** model and approach to aid in teaching problem analysis. This approach encourages students to think of basic skills, such as converting between grams and moles, as tools that can be combined in various ways to solve more complex problems. Students and instructors have responded positively to this concept in earlier editions and we continue to employ this strategy in problem analysis. Tools are identified by an icon in the margin when they are introduced in a chapter and the tools are summarized at the end of each chapter.



TOOLS **Tools for Problem Solving** The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Criteria for a balanced ionic ionic equation (page 164)
To be balanced, an equation that includes the formulas of ions must satisfy the following two criteria: (1) the number of atoms of each kind must be the same on both sides of the equation, and (2) the net electrical charge shown on each side of the equation must be the same.

Ionization of an acid in water (page 165)
Equation 5.2 describes how an acid reacts with water to form hydronium ion plus an anion.

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

Use this tool to write equations for the ionizations of acids and to determine the formulas of the anions formed when the acid molecules lose H^+. The equation also applies to acid anions such as HSO_4^-, which gives SO_4^{2-} when it loses an H^+. Often H_2O is omitted from the equation and the hydronium ion is abbreviated as H^+.

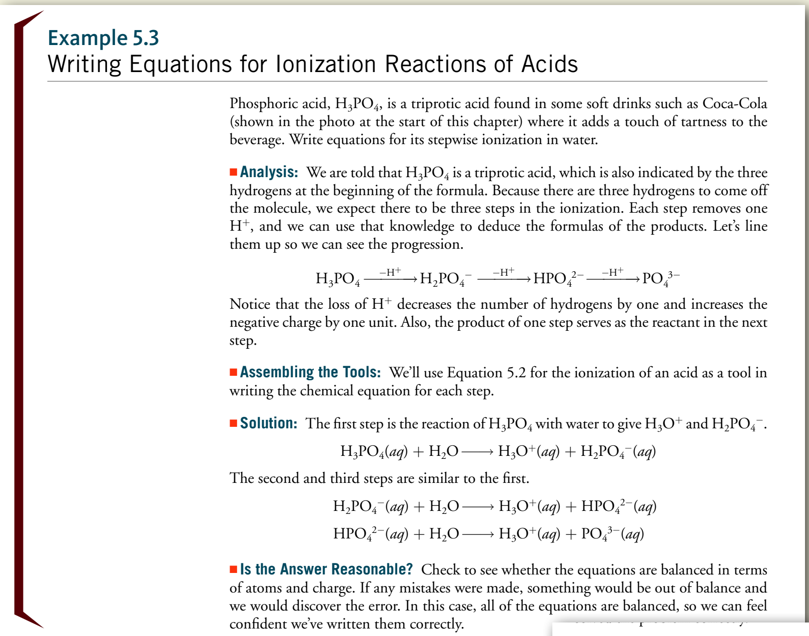
Ionization of a molecular base in water (page 165)
Equation 5.3 describes how molecules of a molecular base acquire H^+ from H_2O to form a cation plus a hydroxide ion.

$$B + H_2O \longrightarrow BH^+ + OH^-$$

Use this tool to write equations for the ionizations of bases and to determine the formula of the cation formed when a base molecule gains an H^+. *Molecular bases are weak and are not completely ionized.*

List of strong acids (page 170)
Formulas of the most common strong acids are given here. If you learn this list and encounter an acid that's *not* on the list, you can assume it is a weak acid. The most common strong acids are HCl, HNO_3, and H_2SO_4. *Remember that strong acids are completely ionized in water.*

- A significant strength of the 5th edition was the three-step process of ***Analysis, Solution,*** and asking ***Is the Answer Reasonable?,*** which was applied to all worked examples. We have now expanded this to include a fourth step called ***Assembling the Tools,*** which appears just following the *Analysis* step. Now, after analyzing the problem and defining the approach to obtain an answer, we describe specifically the tools that will be used in the *Solution* step that comes next. This reinforces the notion that tools can be combined in various ways to solve more complex problems



Example 5.3

Writing Equations for Ionization Reactions of Acids

Phosphoric acid, H_3PO_4, is a triprotic acid found in some soft drinks such as Coca-Cola (shown in the photo at the start of this chapter) where it adds a touch of tartness to the beverage. Write equations for its stepwise ionization in water.

Analysis: We are told that H_3PO_4 is a triprotic acid, which is also indicated by the three hydrogens at the beginning of the formula. Because there are three hydrogens to come off the molecule, we expect there to be three steps in the ionization. Each step removes one H^+, and we can use that knowledge to deduce the formulas of the products. Let's line them up so we can see the progression.

$$H_3PO_4 \xrightarrow{-H^+} H_2PO_4^- \xrightarrow{-H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$$

Notice that the loss of H^+ decreases the number of hydrogens by one and increases the negative charge by one unit. Also, the product of one step serves as the reactant in the next step.

Assembling the Tools: We'll use Equation 5.2 for the ionization of an acid as a tool in writing the chemical equation for each step.

Solution: The first step is the reaction of H_3PO_4 with water to give H_3O^+ and $H_2PO_4^-$.

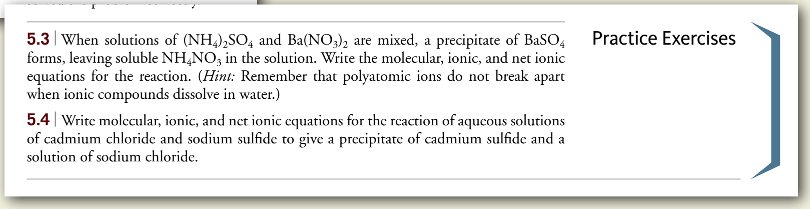
$$H_3PO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + H_2PO_4^-(aq)$$

The second and third steps are similar to the first.

$$H_2PO_4^-(aq) + H_2O \longrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O \longrightarrow H_3O^+(aq) + PO_4^{3-}(aq)$$

Is the Answer Reasonable? Check to see whether the equations are balanced in terms of atoms and charge. If any mistakes were made, something would be out of balance and we would discover the error. In this case, all of the equations are balanced, so we can feel confident we've written them correctly.

- We continue to provide **Practice Exercises** following the worked examples that give the student an opportunity to apply the principles used to solve the preceding example. These have been thoroughly reviewed and in some cases expanded. The answers to all of the Practice Exercises are available to the student in Appendix B at the back of the book.

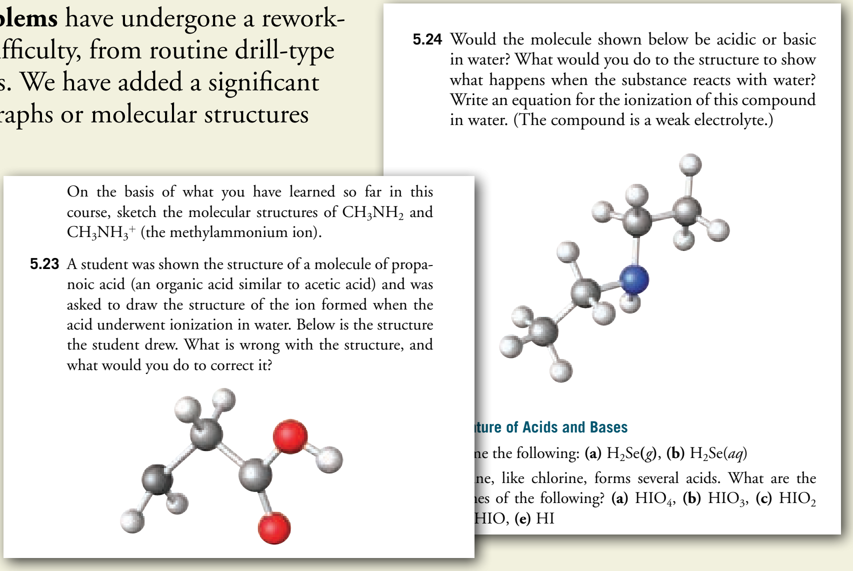


Practice Exercises

5.3 | When solutions of $(NH_4)_2SO_4$ and $Ba(NO_3)_2$ are mixed, a precipitate of $BaSO_4$ forms, leaving soluble NH_4NO_3 in the solution. Write the molecular, ionic, and net ionic equations for the reaction. (*Hint:* Remember that polyatomic ions do not break apart when ionic compounds dissolve in water.)

5.4 | Write molecular, ionic, and net ionic equations for the reaction of aqueous solutions of cadmium chloride and sodium sulfide to give a precipitate of cadmium sulfide and a solution of sodium chloride.

- The **end-of-chapter Questions and Problems** have undergone a reworking to ensure that they provide a range of difficulty, from routine drill-type problems to significantly more difficult ones. We have added a significant number of "visual" problems that include graphs or molecular structures that need to be explained or manipulated. Many problems require students to draw on knowledge acquired in earlier chapters. For example, in many of the problems in Chapter 4 and beyond, the chemical name of a compound in question is given rather than the formula, so students must apply (and review if necessary) the rules of nomenclature presented in Chapter 3.



5.24 Would the molecule shown below be acidic or basic in water? What would you do to the structure to show what happens when the substance reacts with water? Write an equation for the ionization of this compound in water. (The compound is a weak electrolyte.)

On the basis of what you have learned so far in this course, sketch the molecular structures of CH_3NH_2 and $CH_3NH_3^+$ (the methylammonium ion).

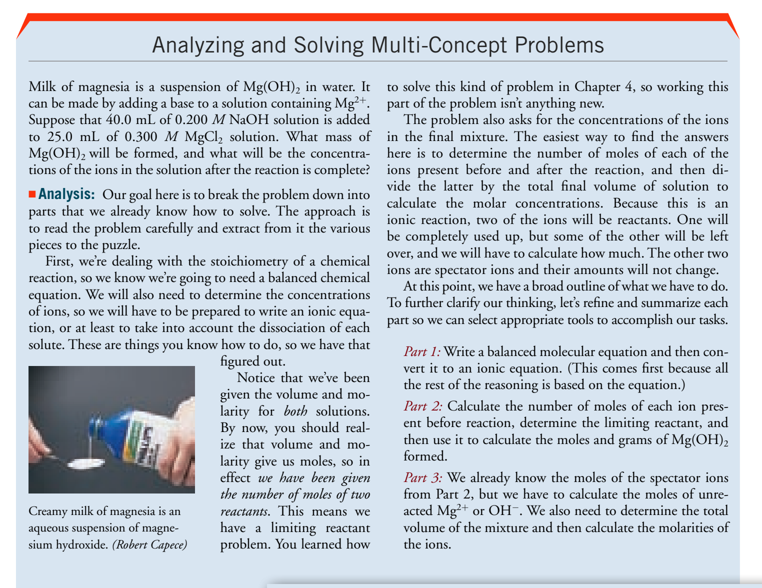
5.23 A student was shown the structure of a molecule of propanoic acid (an organic acid similar to acetic acid) and was asked to draw the structure of the ion formed when the acid underwent ionization in water. Below is the structure the student drew. What is wrong with the structure, and what would you do to correct it?

ture of Acids and Bases

ne the following: **(a)** $H_2Se(g)$, **(b)** $H_2Se(aq)$

ne, like chlorine, forms several acids. What are the
es of the following? **(a)** HIO_4, **(b)** HIO_3, **(c)** HIO_2
HIO, **(e)** HI

- One of the main goals of chemistry instruction is to help students develop the ability to solve problems that are more thought-provoking than typical review problems. Recognizing that students often have difficulty with solving problems that require application of several different concepts, we have introduced a new feature in our teaching arsenal called ***Analyzing and Solving Multi-Concept Problems.*** These problems are more difficult than those in a typical Worked Example and frequently require the use of concepts presented in more than one chapter. Students must combine two or more concepts before reaching a solution, and they must reduce a complex problem into a sum of simpler parts. Problems of this type first appear in Chapter 5 after students have had a chance to work on basic problem skills and after sufficient concepts have been introduced in earlier chapters to make such problems meaningful. ***Analyzing and Solving Multi-Concept Problems*** addresses instructor frustration and students' deficiencies in problem solving by teaching students how to de-construct problemsand **emphasize the thinking** that goes into solving problems.
- The end-of-chapter Problems are categorized to assist instructors in selecting homework. They range in difficulty and include critical thinking and multi-concept problems.
- Following groups of approximately three or four chapters we include problem sets titled ***Bringing it Together*** that consist mostly of problems that require students to apply concepts developed in two or more of the preceding chapters. Problems have been selected to provide a range of difficulties so as to challenge students of varying levels of achievement.



Analyzing and Solving Multi-Concept Problems

Milk of magnesia is a suspension of $Mg(OH)_2$ in water. It can be made by adding a base to a solution containing Mg^{2+}. Suppose that 40.0 mL of 0.200 *M* NaOH solution is added to 25.0 mL of 0.300 *M* $MgCl_2$ solution. What mass of $Mg(OH)_2$ will be formed, and what will be the concentrations of the ions in the solution after the reaction is complete?

Analysis: Our goal here is to break the problem down into parts that we already know how to solve. The approach is to read the problem carefully and extract from it the various pieces to the puzzle.

First, we're dealing with the stoichiometry of a chemical reaction, so we know we're going to need a balanced chemical equation. We will also need to determine the concentrations of ions, so we will have to be prepared to write an ionic equation, or at least to take into account the dissociation of each solute. These are things you know how to do, so we have that figured out.

Notice that we've been given the volume and molarity for *both* solutions. By now, you should realize that volume and molarity give us moles, so in effect *we have been given the number of moles of two reactants*. This means we have a limiting reactant problem. You learned how to solve this kind of problem in Chapter 4, so working this part of the problem isn't anything new.

Creamy milk of magnesia is an aqueous suspension of magnesium hydroxide. *(Robert Capece)*

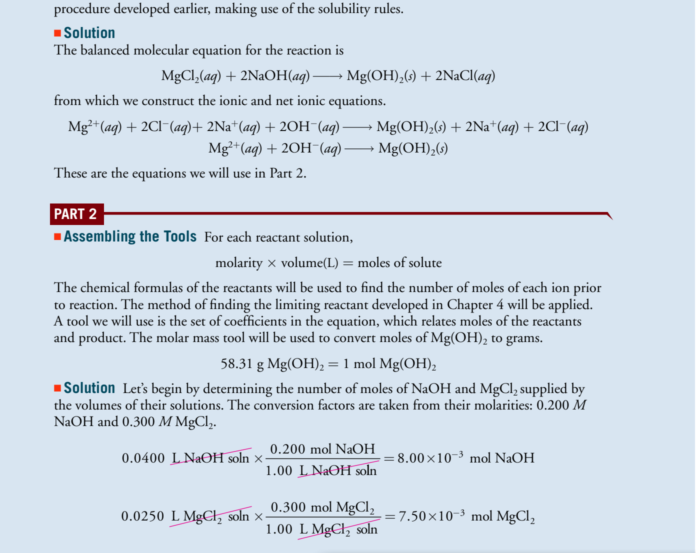
The problem also asks for the concentrations of the ions in the final mixture. The easiest way to find the answers here is to determine the number of moles of each of the ions present before and after the reaction, and then divide the latter by the total final volume of solution to calculate the molar concentrations. Because this is an ionic reaction, two of the ions will be reactants. One will be completely used up, but some of the other will be left over, and we will have to calculate how much. The other two ions are spectator ions and their amounts will not change.

At this point, we have a broad outline of what we have to do. To further clarify our thinking, let's refine and summarize each part so we can select appropriate tools to accomplish our tasks.

Part 1: Write a balanced molecular equation and then convert it to an ionic equation. (This comes first because all the rest of the reasoning is based on the equation.)

Part 2: Calculate the number of moles of each ion present before reaction, determine the limiting reactant, and then use it to calculate the moles and grams of $Mg(OH)_2$ formed.

Part 3: We already know the moles of the spectator ions from Part 2, but we have to calculate the moles of unreacted Mg^{2+} or OH^-. We also need to determine the total volume of the mixture and then calculate the molarities of the ions.



PART 1

Assembling the Tools We need to set up a metathesis equation and balance it. We follow the procedure developed earlier, making use of the solubility rules.

Solution

The balanced molecular equation for the reaction is

$$MgCl_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$$

from which we construct the ionic and net ionic equations.

$$Mg^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$$

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$$

These are the equations we will use in Part 2.

PART 2

Assembling the Tools For each reactant solution,

$$\text{molarity} \times \text{volume(L)} = \text{moles of solute}$$

The chemical formulas of the reactants will be used to find the number of moles of each ion prior to reaction. The method of finding the limiting reactant developed in Chapter 4 will be applied. A tool we will use is the set of coefficients in the equation, which relates moles of the reactants and product. The molar mass tool will be used to convert moles of $Mg(OH)_2$ to grams.

$$58.31 \text{ g } Mg(OH)_2 = 1 \text{ mol } Mg(OH)_2$$

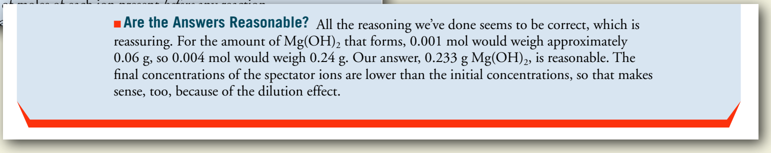
Solution Let's begin by determining the number of moles of NaOH and $MgCl_2$ supplied by the volumes of their solutions. The conversion factors are taken from their molarities: 0.200 *M* NaOH and 0.300 *M* $MgCl_2$.

$$0.0400 \ \cancel{\text{L NaOH soln}} \times \frac{0.200 \text{ mol NaOH}}{1.00 \ \cancel{\text{L NaOH soln}}} = 8.00 \times 10^{-3} \text{ mol NaOH}$$

$$0.0250 \ \cancel{\text{L } MgCl_2 \text{ soln}} \times \frac{0.300 \text{ mol } MgCl_2}{1.00 \ \cancel{\text{L } MgCl_2 \text{ soln}}} = 7.50 \times 10^{-3} \text{ mol } MgCl_2$$

From this information, we obtain the number

occurs. In doing this, notice that we take into a



Are the Answers Reasonable? All the reasoning we've done seems to be correct, which is reassuring. For the amount of $Mg(OH)_2$ that forms, 0.001 mol would weigh approximately 0.06 g, so 0.004 mol would weigh 0.24 g. Our answer, 0.233 g $Mg(OH)_2$, is reasonable. The final concentrations of the spectator ions are lower than the initial concentrations, so that makes sense, too, because of the dilution effect.

Reinforcing Problem-solving Skills and Student Comprehension with *WileyPLUS*

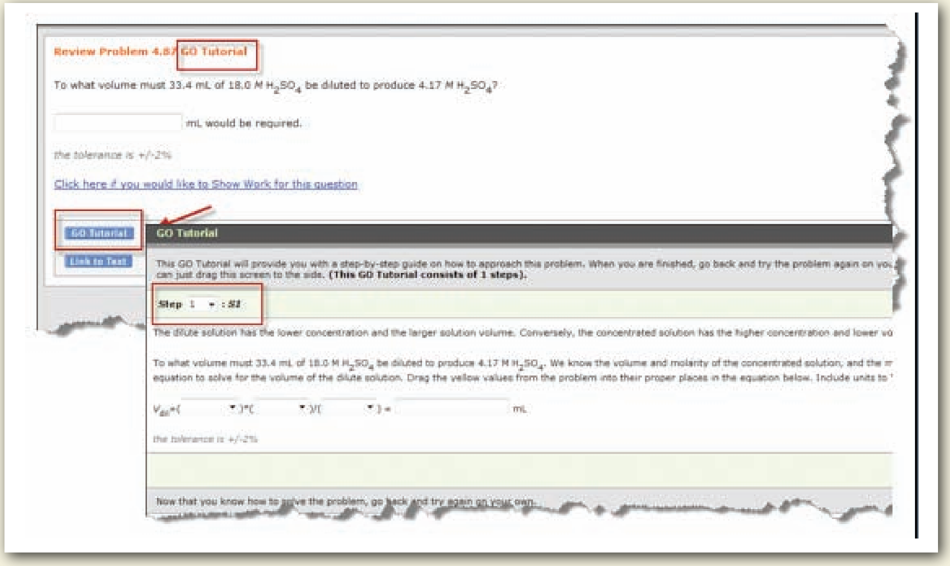
We have strived to provide a seamless, total solution to the challenges of the general chemistry course with this edition, fully combining the development of the textbook content with the media and resources delivered within ***WileyPLUS,*** an innovative, research-based online environment designed for both effective teaching and learning. ***WileyPLUS*** for ***Chemistry: The Molecular Nature of Matter,*** **Sixth Edition** provides depth and breadth of assessment that is fully *integrated* with the learning content. The author team has carefully crafted the assessment content in ***WileyPLUS*** to directly correlate to the printed text … creating a synergy between text and online resources in ***WileyPLUS.***

WileyPLUS was designed to facilitate dynamic learning and retention of learned concepts by promoting conceptual understanding and visualization of chemical phenomena at the undergraduate level. Assessment in ***WileyPLUS*** is offered in four unique question banks: practice questions, end-of-chapter questions, test bank, and concept mastery assignments. All assessment questions offer immediate feedback and online grading along with varying levels of question assistance.

Research-Based Design

WileyPLUS provides an online environment that integrates relevant resources, including the entire digital textbook, in an easy-to-navigate framework. The design of ***WileyPLUS*** makes it easy for students to know **what** it is they need to do, boosting their confidence and preparing them for greater engagement in class and lab. Concept Modules, Activities, Self Study and Progress Checks in ***WileyPLUS*** will ensure that students know **how** to study effectively so they will remain engaged and stay on task.

- In ***WileyPLUS***, all **Analyzing Multiple Concept Problems** are complemented by an Office Hours video, which is a video in which an instructor narrates the problem solving steps as the student watches those steps executed in a white board environment, and a Guided Online Tutorial, which is an interactive version of the problem presented. In the Guided Online Tutorial, the student has an opportunity to work through a version of the problem themselves, and is provided with feedback on each part of the answer they submit.



Review Problem 4.87 GO Tutorial

To what volume must 33.4 mL of 18.0 *M* H_2SO_4 be diluted to produce 4.17 *M* H_2SO_4?

mL would be required.

the tolerance is +/-2%

Click here if you would like to Show Work for this question

This GO Tutorial will provide you with a step-by-step guide on how to approach this problem. When you are finished, go back and try the problem again on you
can just drag this screen to the side. **(This GO Tutorial consists of 1 steps).**

Step 1 : S1

The dilute solution has the lower concentration and the larger solution volume. Conversely, the concentrated solution has the higher concentration and lower vo

To what volume must 33.4 mL of 18.0 M H_2SO_4 be diluted to produce 4.17 M H_2SO_4. We know the volume and molarity of the concentrated solution, and the m
equation to solve for the volume of the dilute solution. Drag the yellow values from the problem into their proper places in the equation below. Include units to

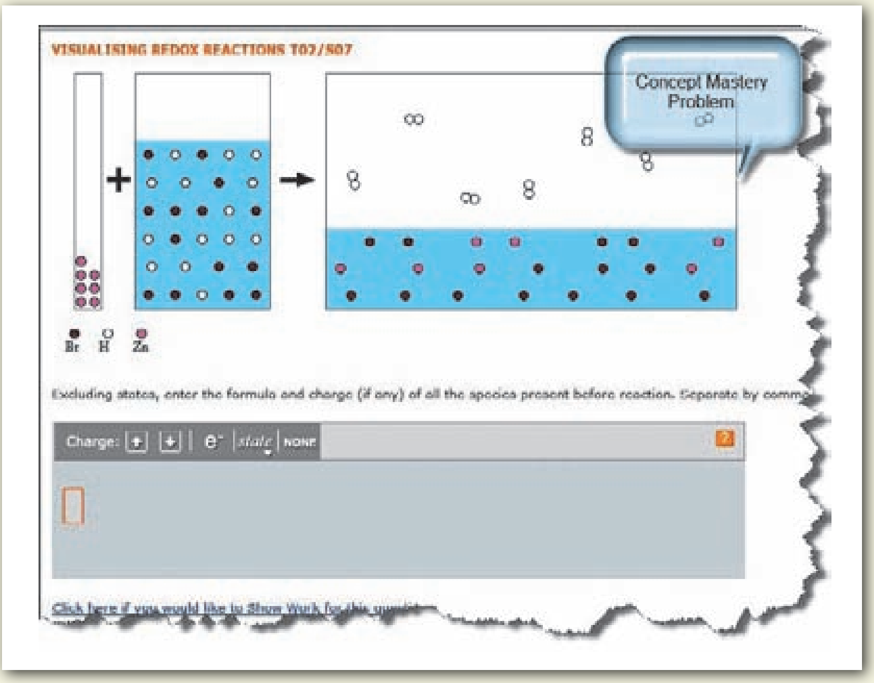
V_{dil}=( )*( )/( ) = mL

the tolerance is +/-2%

Now that you know how to solve the problem, go back and try again on your own.

Student Assessment and Concept Mastery

An important part of teaching is student assessment. The prebuilt **Concept Mastery** assignments in ***WileyPLUS*** http://www.wiley.com/college/sc/jespersen facilitate dynamic learning and retention of learned concepts by promoting conceptual understanding and visualization of chemical phenomena. **Concept Mastery** assignments have multiple levels of parameterization and test key concepts from multiple points of view (visual, symbolic, graphical, quantitative). Each student receives a unique assignment and must achieve a default mastery threshold to receive full points for the assignment.



VISUALISING REDOX REACTIONS T02/S07

Excluding states, enter the formula and charge (if any) of all the species present before reaction. Separate by comm

Click here if you would like to Show Work for this

Instructor Resources

WileyPLUS provides reliable, customizable resources that reinforce course goals inside and outside the classroom as well as visibility into individual student progress. Pre-created materials and activities help instructors optimize their time:

Customizable Course Plan: ***WileyPLUS*** comes with a pre-created Course Plan designed by a subject matter expert uniquely for this course. Simple drag-and-drop tools make it easy to assign the course plan as is or modify it to reflect your course syllabus.

Pre-created Activity Types Include:

- Questions
- Readings and resources
- Concept Mastery

Course Materials and Assessment Content:

- PowerPoint Slides
- Classroom Response System (Clicker) Questions
- Instructor's Manuals
- Assessment consisting of Gradable Practice Questions (embedded with online text)
- Question Assignments
- End-of-chapter problems coded algorithmically with hints
- Links to text
- Instructor-controlled problem-solving help
- Prebuilt Concept Mastery Assignments
- Test Bank

For more information about ***WileyPLUS*** go to www.wileyplus.com.

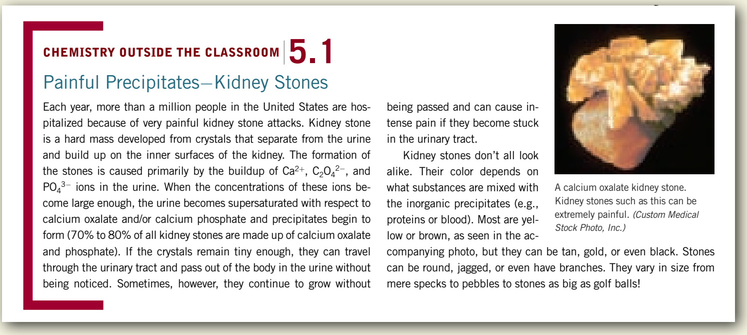
Significant Changes in the 6th Edition

As noted earlier, our mission in developing this revision was to sharpen the focus of the text as it relates to the relationship between behavior at the molecular level and properties observed at the macroscopic level.

As much as possible, chapters are written to stand alone as instructional units, enabling instructors to modify the chapter sequence to suit the specific needs of their students. For example, if an instructor wishes to cover the chapter dealing with the properties of gases (Chapter 11) early in the course, they can easily do so. While we believe this chapter fits best in sequence with the chapters dealing with the other states of matter, we realize that there are other valid organizational preferences and the chapter has been written to accommodate them.

Some of the more significant changes to the organization are the following:

- Special topics consisting of short essays are spread throughout the book. Those titled ***Chemistry Outside the Classroom*** and ***Chemistry and Current Affairs*** provide descriptions of real-world, practical applications of chemistry to industry, medicine, and the environment. Essays titled ***On the Cutting Edge*** serve to highlight chemical phenomena that are of current research interest and that have potential practical applications in the future. A list of these special topics appears at the end of the Table of Contents.



CHEMISTRY OUTSIDE THE CLASSROOM | 5.1

Painful Precipitates—Kidney Stones

Each year, more than a million people in the United States are hospitalized because of very painful kidney stone attacks. Kidney stone is a hard mass developed from crystals that separate from the urine and build up on the inner surfaces of the kidney. The formation of the stones is caused primarily by the buildup of Ca^{2+}, $C_2O_4^{2-}$, and PO_4^{3-} ions in the urine. When the concentrations of these ions become large enough, the urine becomes supersaturated with respect to calcium oxalate and/or calcium phosphate and precipitates begin to form (70% to 80% of all kidney stones are made up of calcium oxalate and phosphate). If the crystals remain tiny enough, they can travel through the urinary tract and pass out of the body in the urine without being noticed. Sometimes, however, they continue to grow without being passed and can cause intense pain if they become stuck in the urinary tract.

Kidney stones don't all look alike. Their color depends on what substances are mixed with the inorganic precipitates (e.g., proteins or blood). Most are yellow or brown, as seen in the accompanying photo, but they can be tan, gold, or even black. Stones can be round, jagged, or even have branches. They vary in size from mere specks to pebbles to stones as big as golf balls!

A calcium oxalate kidney stone. Kidney stones such as this can be extremely painful. *(Custom Medical Stock Photo, Inc.)*

- **Chapter 1** is entirely new and sets the tone for the rest of the text. It provides an introduction to the atomic theory and the concepts of atoms, molecules, elements, and compounds. A clear connection is made between observations at the macroscopic level and their interpretation at the molecular level. We introduce chemical symbols and their use in representing atoms of elements. Ball-and-stick and space-filling representations of molecules are introduced, and students are taught to associate molecular structures with chemical formulas. The concepts of chemical reactions and chemical equations are presented and described by drawings of molecules and through the use of chemical symbols. The laws of definite proportions, conservation of mass, and multiple proportions are described and interpreted in molecular terms. All of this is done clearly and prepares students for the more in-depth treatments of these subjects in the chapters that follow. End-of-chapter exercises include concept questions that ask students to describe and interpret molecular structures and chemical changes.

- **Chapter 2** is devoted to measurements and their units. The importance of quantitative measurements with respect to physical properties is introduced along with the concepts of intensive and extensive properties. The uncertainty of measurements is described. Significant figures are developed to provide the student with a logical method for assessing data. Finally, the method of dimensional analysis is discussed and applied to familiar calculations to develop confidence at an early stage. Color-coded cancellations are used to help the student understand the process.

- **Chapter 3** provides students with their first exploration of the internal structures of atoms. We now include the history of the discovery of subatomic particles within the body of the chapter. We continue to divide chemical nomenclature into sections that deal separately with molecular and ionic compounds. From experience, we have found that students are able to digest these topics more easily when presented in manageable chunks. To drive home the importance of chemical nomenclature, students are required to construct formulas from names in homework problems in later chapters.

- **Chapter 4** covers the mole concept and stoichiometry. The discussions have been carefully revised where necessary, with molecular diagrams being used to relate stoichiometric principles on the molecular level to mole-sized quantities. Dimensional analysis with color-coded cancel marks is used rigorously for all examples.
- **Chapter 5** focuses on ionic reactions in aqueous solutions and includes additional molecular diagrams depicting solution formation and solution concentration as well as in exercises. Molarity is introduced and used in stoichiometry calculations involving solutions. In this chapter we introduce students to our new feature, *Analyzing and Solving Multi-Concept Problems*.
- **Chapter 6** deals with redox reactions and includes a revised set of rules for assigning oxidation numbers. The change is aimed at making it easier for the student to apply the rules. Illustrations for a variety of oxidation-reduction processes have changed to include molecular diagrams illustrating the changes that take place at the atomic scale.
- **Chapter 7** covers thermochemistry and has been carefully revised with the addition of more illustrations. The manner in which potential energy changes are illustrated has been modified to increase clarity.
- **Chapter 8** is a logical extension of Chapter 3 in our discussion of how our understanding of the atom has developed. The fundamentals of the quantum mechanical atom are introduced to the extent that the material is relevant to the remainder of the text. The discussion has been updated with some tweaking to improve clarity along with some additional illustrations.
- **Chapter 9,** the first of two chapters dealing with chemical bonding, now includes a more thorough discussion of lattice energy and its influence on the formation of ionic compounds. After the introduction of covalent bonding, we now include a separate *brief* section devoted to some common kinds of organic compounds. These are substances students encounter in discussions of physical and chemical properties in later chapters. The section also serves as a brief introduction to organic chemistry for students whose major requires only one semester of chemistry. For instructors who do not wish to discuss organic compounds at this point in the course, the section is easily skipped. Section 9.7 provides a discussion of the reducing properties of elements in Groups 1A and 2A, and the oxidizing power of the nonmetallic elements. This permits a timely discussion of the influence of electronegativity on chemical reactivity.
- **Chapter 10,** the second bonding chapter, now includes a discussion of the way the algebraic signs of atomic orbitals determine the formation of bonding and antibonding molecular orbitals. We also include a section on the bonding in solids as well as a section that discusses the influence of atomic size on the ability of atoms to form pi bonds. For the latter, we examine how multiple bond formation influences the molecular structures of the elemental nonmetals.
- **Chapter 11,** which deals with the properties of gases, now includes a brief section on the chemistry of the atmosphere and the concepts behind global energy transfer. A section on modern pressure sensors and transducers has also been added.
- **Chapter 12** covers intermolecular forces and their effects on physical properties of liquids and solids. Some topics have been rearranged to give a more logical topic flow. Calculations involving the Clausius-Clapeyron equation now appear in the main body of the text, rather than as a special topic.

- **Chapter 13** discusses the physical properties of solutions. Diagrams showing Raoult's law for non-ideal solutions have been added. We've also added a section on heterogeneous mixtures that includes a discussion of colloids. The issue of potable water provided by reverse osmosis has been added. The concept of incremental heats of solution is introduced.

- **Chapter 14** covers the kinetics of chemical reactions, including mechanisms, and catalysis. The section on instantaneous rates of reactions has been expanded, and the integrated zero order rate law has been added.

- **Chapter 15** is the first of several chapters devoted to chemical equilibria. Changes to this chapter have been relatively minor. We have concentrated on developing the equilibrium concept at the molecular level and on polishing the worked examples to make them more accessible to the student.

- **Chapter 16,** which examines acid-base chemistry theories, concludes with a treatment of modern ceramic materials prepared by the sol-gel process. This discussion illustrates how simple acid-base chemistry can be applied to the production of modern materials.

- **Chapter 17** treats acid-base equilibria and calculations of pH in detail. Included are detailed examples of pH calculations involving strong and weak acids and bases, buffers and polyprotic acids. Interrelationships based on the Brønsted-Lowry theory are developed. Titration curves, including polyprotic acid titrations, are discussed. Use of simplifying assumptions is based on fundamental principles.

- **Chapter 18,** the final chapter on equilibria, deals with solubility and simultaneous equilibria. This chapter continues the strong emphasis on solving equilibrium problems developed in the previous chapters. We have included a section on qualitative analysis of metal ions, and we continue to introduce complex ions in this chapter because they participate in equilibria.

- **Chapter 19** presents the fundamentals of thermodynamics and includes discussions of the first, second, and third laws. Entropy and Gibbs free energy are introduced, and examples using the concept of state functions are presented with detailed solutions. New special topics on entropy and thermodynamics of sustainability are introduced.

- **Chapter 20** discusses the two fundamental electrochemical processes: electrolysis, and the use of galvanic (voltaic) cells to produce external electron flow. Unambiguous electrochemical cells are always presented. Details of the relationships between $\Delta G°$, $E°_{\text{cell}}$ and K_{eq} are presented with detailed examples.

- **Chapter 21** discusses nuclear reactions and their applications. In this chapter, we have incorporated current research on carbon-14 dating and included a new table that summarizes the nuclear reactions.

- **Chapter 22** is devoted entirely to the study of metal complexes. We have removed from this chapter the material devoted to the nonmetals and metalloids that was present in Chapter 21 of the 5th edition. Some of the topics have been distributed into earlier chapters where it seemed to be appropriate.

- **Chapter 23** provides an expanded discussion of organic chemistry. It has undergone significant restructuring and rewriting, both to shorten the chapter and to take into account the introduction to organic chemistry provided in Chapter 9.

Teaching and Learning Resources

A comprehensive package of supplements has been created to assist both the teacher and the student and includes the following:

For Students

Study Guide by Neil Jespersen of St. John's University. This guide has been written to further enhance the understanding of concepts. It is an invaluable tool for students and contains chapter overviews, additional worked-out problems giving detailed steps involved in solving them, alternate problem-solving approaches, as well as extensive review exercises. (ISBN: 978-0-470-57772-1)

Solutions Manual by Duane Swank, of Pacific Lutheran University, with contributions by Alison Hyslop of St. John's University. The manual contains worked-out solutions for text problems whose answers appear in Appendix B. (ISBN: 978-0-470-57773-8)

Laboratory Manual for Principles of General Chemistry, 9th Edition, by Jo Beran of Texas A&M University, Kingsville. This comprehensive laboratory manual is for use in the general chemistry course. This manual is known for its broad selection of topics and experiments, and for its clear, user-friendly layout and design. Containing enough material for two or three terms, this lab manual emphasizes techniques, helping students learn the appropriate time and situation for their correct use. The accompanying Instructor's Manual presents the details of each experiment, including overviews, an instructor's lecture outline, and teaching hints. The Instructor's Manual also contains answers to the pre-laboratory assignment and laboratory questions. (ISBN: 978-0-470-64789-9)

For Instructors

Instructor's Manual by Scott Kirkby of East Tennessee State University. In addition to lecture outlines, alternate syllabi, and chapter overviews, this manual contains suggestions for small group active-learning projects, class discussions, tips for first-time instructors, class demonstrations, short writing projects, and contains relevant web links for each chapter.

Test Bank by Donovan Dixon of the University of Central Florida and Justin Meyer of South Dakota School of Mines and Technology. The Test Bank contains over 2000 questions including: multiple-choice, true-false, short answer questions, fill in the blank questions, and critical thinking problems. PC- and Macintosh-compatible versions of the entire test bank are available with full editing features to help the instructor customize tests.

Instructor's Solutions Manual by Duane Swank, of Pacific Lutheran University, with contributions by Alison Hyslop, of St. John's University, contains worked-out solutions to all end of chapter problems.

Digital Image Archive—Text web site includes downloadable files of text images in JPEG format. Instructors may use these images to customize their presentations and to provide additional visual support for quizzes and exams.

PowerPoint Lecture Slides by Elise Megehee, of St. John's University, feature images from the text on slides that are customizable to fit your course.

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1 Chemistry and the Atomic/Molecular View of Matter

Chapter Outline

1.1 | Chemistry and Its Place among the Sciences

1.2 | Laws and Theories: The Scientific Method

1.3 | Matter and Its Classifications

1.4 | Dalton and the Atomic Theory

1.5 | Atoms and Molecules and Chemical Formulas

1.6 | Chemical Reactions and Chemical Equations

The girl listening to music on her iPod probably isn't thinking much about chemistry, but if it were not for the inventions made possible by chemical discoveries there would be no music to fill her spare time. In this chapter you begin your study of a science that affects your life every single day. As you progress through your chemistry course, we hope you enjoy learning about how the properties of atoms and molecules affects the world in which you live. Granger Wootz/Getty Images, Inc.

This Chapter in Context

It's quite likely that you have an iPod, just like the young woman shown in the photo on the preceding page. This wonderful device is only one of a multitude of gadgets that enrich our lives. But if it were not for the science of chemistry, almost none of the materials used to make them, such as their plastic cases and electronic components, would exist. Even clothing made from "natural" fibers such as cotton or wool may be colored with synthetic dyes and sewn together with thread made of synthetic fibers. Chemistry affects our lives every day in countless ways, and one of our goals in this book is to give you an appreciation for the significant role that chemistry plays in modern society.

In this first chapter we present some fundamental concepts and definitions that we will use throughout the book. We also discuss how the theory of atoms came about, how the concept of atoms is used to describe chemical substances and chemical change, and how we will represent atoms and their combinations visually in later discussions. If you've had a prior course in chemistry, you're probably familiar with most of the topics that we cover here. Nevertheless, it is important to be sure that you have a mastery of these subjects, because we will use them frequently in the chapters ahead.

Clothing in a dazzling array of colors is possible because of synthetic dyes discovered by chemists. *(Getty Images, Inc.)*

1.1 | Chemistry and Its Place among the Sciences

■ In our discussions, we do not assume that you have had a prior course in chemistry. However, even if some of the subjects discussed here are familiar, we urge you to study this chapter thoroughly, because the concepts developed here will be used in later chapters.

Chemistry[1] can be defined as *the study of the composition, properties, and transformations of matter*. This includes all of the chemicals that make up the tangible things in our world. In their studies, chemists seek answers to fundamental questions about how the composition of a substance affects its properties. With such knowledge comes the possibility of designing materials with specifically intended characteristics. Underlying all of this is a search for knowledge about the way the structure of matter at the atomic level is related to the behavior of substances that we observe through our senses.

Chemistry is particularly concerned with the way substances change, often dramatically, when they interact with each other in *chemical reactions*. By understanding such changes at a fundamental level, chemists have been able to create materials never before found on earth—materials with especially desirable properties that fulfill specific needs of society. For example, synthetic plastics, ceramics, and metal alloys now permit engineers and architects to build structures that would never have been possible using only naturally occurring materials. Knowledge of fundamental aspects of chemical reactions has also enabled biologists to develop a fundamental understanding of many of the processes taking place in living organisms.

Because of its broad scope, chemistry touches all of the sciences, which is why some have called it the central science. In fact, the involvement of chemistry among the various branches of science is reflected in the names of some of the divisions of the American Chemical Society, the largest scientific organization in the world (see Table 1.1). Although you may not plan to be a chemist, some knowledge of chemistry will surely be valuable to you.

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[1] Important terms are set in bold type to call them to your attention. Be sure you learn their meanings. If you need to review them, they are also in the Glossary at the back of the book.

Table 1.1 Names of Some of the Divisions of the American Chemical Society

Agricultural & Food Chemistry
Agrochemicals
Biochemical Technology
Biological Chemistry
Business Development & Management
Carbohydrate Chemistry
Cellulose, Paper & Textile
Chemical Health & Safety
Chemical Toxicology
Chemistry & the Law
Colloid & Surface Chemistry
Computers in Chemistry
Environmental Chemistry
Fertilizer & Soil Chemistry
Fuel Chemistry
Geochemistry
Industrial & Engineering Chemistry
Medicinal Chemistry
Nuclear Chemistry & Technology
Petroleum Chemistry
Polymer Chemistry
Polymeric Materials: Science & Engineering
Rubber

1.2 | Laws and Theories: The Scientific Method

You've probably spent some time playing video games, so you know that you learn a game by trial and error. You try one thing and get shot down, so next time you try something else. Gradually you get to know how to get through all the traps and can fight your way to the finish. Your actions in game playing are not far removed from the way scientists approach the study of the world around them.

Scientists are curious creatures who want to know what makes the world "tick." The approach they take to their work is generally known as the **scientific method.** Basically it boils down to gathering information and formulating explanations.

■ Roger Bacon, a thirteenth century philosopher, is credited as the first to suggest that experimental observations must be the basis of modern science.

In the sciences, we usually gather information by performing experiments in laboratories under controlled conditions so the observations we make are reproducible (Figure 1.1). An **observation** is a statement that accurately describes something we see, hear, taste, feel, or smell. The observations we make while performing experiments are referred to as **data**.

Figure 1.1 | **A research chemist working in a modern laboratory.** Reproducible conditions in a laboratory permit experiments to yield reliable results. *(©AP/Wide World Photos)*

Data gathered during an experiment often lead us to draw conclusions. A **conclusion** is a statement that's based on what we think about a series of observations. For example, consider the following statements about the fermentation of grape juice to make wine:

1. Before fermentation, grape juice is very sweet and contains no alcohol.
2. After fermentation, the grape juice is no longer as sweet and it contains a great deal of alcohol.
3. In fermentation, sugar is converted into alcohol.

Statements 1 and 2 are observations because they describe properties of the grape juice that can be tasted and smelled. Statement 3 is a conclusion because it *interprets* the observations that are available.

Experimental Observations and Scientific Laws

One of the goals of science is to organize facts so that relationships or generalizations among the data can be established. For example, if we study the behavior of gases, such as the air we breathe, we soon discover that the volume of a gas depends on a number of factors, including the amount of the gas, its temperature, and its pressure. The observations we record relating these factors are our data.

One generalization we could make by studying data obtained from many experiments performed using different temperatures and pressures is that when the temperature of the gas is held constant, squeezing the gas into half of its original volume causes the pressure of the gas to double. If we were to repeat our experiments many times with numerous *different* gases, we would find that this generalization is uniformly applicable to all of them. Such a broad generalization, based on the results of many experiments, is called a **law** or **scientific law.**

■ The pressure of the gas is *inversely proportional* to its volume, so the smaller the volume, the larger the pressure.

We often express laws in the form of mathematical equations. For example, if we represent the pressure of a gas by the symbol P and its volume by V, the inverse relationship between pressure and volume can be written as

$$P = \frac{C}{V}$$

where C is a proportionality constant. (We will discuss gases and the laws relating to them in greater detail in Chapter 11.)

Hypotheses and Theories: Models of Nature

As useful as they may be, laws only state what happens; they do not provide explanations. *Why*, for example, *are gases so easily compressed to a smaller volume?* More specifically, *what must gases be like at the most basic, elementary level for them to behave as they do*? Answering such questions when they first arise is no simple task and requires much speculation. But over time scientists build mental pictures, called **theoretical models**, that enable them to explain observed laws.

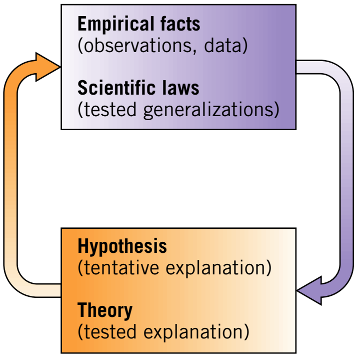

Figure 1.2 | **The scientific method is cyclical.** Observations suggest explanations, which suggest new experiments, which suggest new explanations, and so on.

In the development of a theoretical model, researchers form tentative explanations called **hypotheses** (Figure 1.2). They then perform experiments that test predictions derived from the model. Sometimes the results show that the model is wrong. When this happens, the model must be abandoned or modified to account for the new data. Eventually, if the model survives repeated testing, it achieves the status of a theory. *A* **theory** *is a tested explanation of the behavior of nature.* Keep in mind, however, that it is impossible to perform every test that might show a theory to be wrong, so we can never prove *absolutely* that a theory is correct.

Science doesn't always proceed in the orderly stepwise fashion described above. Luck sometimes plays an important role. For example, in 1828 Frederick Wöhler, a German chemist, was testing one of his theories and obtained an unexpected material when he heated a substance called ammonium cyanate. Out of curiosity he analyzed it and found it to be urea (a component of urine). This was exciting because it was the first time anyone had knowingly made a substance produced only by living creatures from a chemical not having a life origin. The fact that this could be done led to a whole new branch of chemistry called *organic chemistry*. Yet, had it not been for Wöhler's curiosity and his application of the scientific method to his unexpected results, the importance of his experiment might have gone unnoticed.

■ Many breakthrough discoveries in science have come about by accident.

As a final note, it is significant that the most spectacular and dramatic changes in science occur when major theories are proved to be wrong. Although this happens only rarely, when it does occur, scientists are sent scrambling to develop new theories, and exciting new frontiers are opened.

The Atomic Theory as a Model of Nature

Virtually every scientist would agree that the most significant theoretical model of nature ever formulated is the atomic theory, discussed in some detail in Section 1.4. According to this theory, all chemical substances are composed of tiny submicroscopic particles that we call **atoms,** which combine in various ways to form all the complex materials we find in the **macroscopic**, visible world around us. This concept forms the foundation for the way scientists think about nature. The atomic theory and how it enables us to explain chemical facts forms the central theme of this chapter, and much of the rest of this book as well.

■ *Macroscopic* commonly refers to physical objects that are measurable and observable by the naked eye.

1.3 | Matter and Its Classifications

We mentioned above that one of our goals is to be able to relate things we observe around us and in the laboratory to the way individual atoms and their combinations behave at the submicroscopic level. To begin this discussion we need to study how chemistry views the macroscopic world.

Matter Defined

In Section 1.1 we described chemistry as being concerned with the properties and transformations of matter. **Matter** is defined as anything that occupies space and has mass. It is the stuff our universe is made of. All of the objects around us, from rocks to pizza to people, are examples of matter.

Notice that our definition of matter uses the term *mass* rather than *weight*. The words mass and weight are often used interchangeably even though they refer to different things. **Mass** *refers to how much matter there is in a given object*[2], *whereas* **weight** *refers to the force with which the object is attracted by gravity*. For example, a golf ball contains a certain amount of matter and has a certain mass, which is the same regardless of the golf ball's location. However, the *weight* of a golf ball on earth is about six times greater than it would be on the moon because the gravitational attraction of the earth is six times that of the moon. Because mass does not vary from place to place, we use mass rather than weight when we specify the amount of matter in an object. Mass is measured with an instrument called a balance, which we will discuss in Chapter 2.

Elements

Chemistry is especially concerned with **chemical reactions,** which are transformations that alter the chemical compositions of substances. An important type of chemical reaction is **decomposition,** in which one substance is changed into two or more others. For example, if we pass electricity through molten (melted) sodium chloride (salt), the silvery metal sodium and the pale green gas, chlorine, are formed. This change has decomposed sodium chloride into two simpler substances. No matter how we try, however, sodium and chlorine cannot be decomposed further by chemical reactions into still simpler substances that can be stored and studied.

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[2] Mass is a measure of an object's momentum, or resistance to a change in motion. Something with a large mass, such as a truck, contains a lot of matter and is difficult to stop once it's moving. An object with less mass, such as a baseball, is much easier to stop.

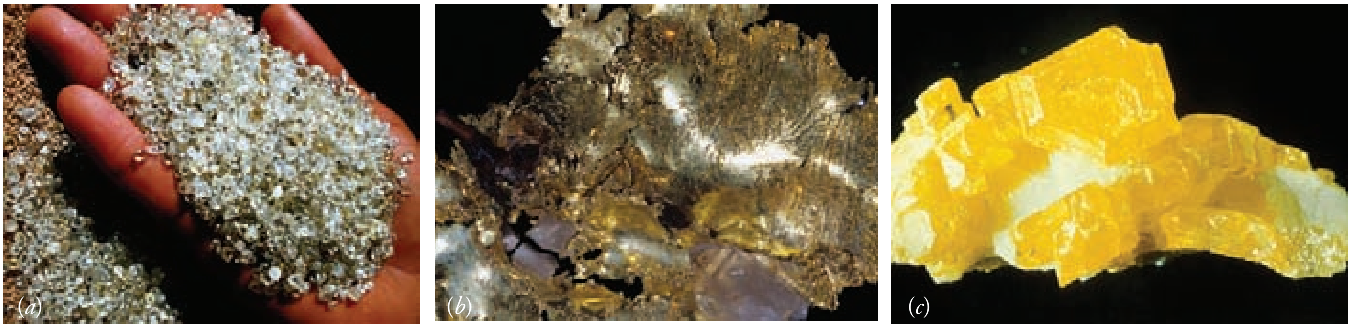

Figure 1.3 | **Some elements that occur naturally.** (*a*) Carbon in the form of diamonds. (Coal is also made up mostly of carbon.) (*b*) Gold. (*c*) Sulfur. *(Peter/Stef Lamberti/GettyImages, Inc.; Ken Lucas/VisualsUnlimited; Manfred Kage/PeterArnold, Inc.)*

In chemistry, *substances that cannot be decomposed into simpler materials by chemical reactions are called* **elements**. Sodium and chlorine are two examples. Others you may be familiar with include iron, aluminum, sulfur, and carbon (as in charcoal and diamonds). Some elements are gases at room temperature. Examples include chlorine, oxygen, hydrogen, nitrogen, and helium. Elements are the simplest forms of matter that chemists work with directly. All more complex substances are composed of elements in various combinations. Figure 1.3 shows some samples of elements that occur uncombined with other elements in nature.

Mountains of the bright yellow element sulfur await shipment on a dock in Vancouver, BC, Canada. The sulfur is extracted from crude oil where it is present as a contaminant that can cause serious air pollution if not removed. *(Courtesy of James Brady)*

Table 1.2 Elements That Have Symbols Derived from Their Latin Names

Element	Symbol	Latin Name
Sodium	Na	Natrium
Potassium	K	Kalium
Iron	Fe	Ferrum
Copper	Cu	Cuprum
Silver	Ag	Argentum
Gold	Au	Aurum
Mercury	Hg	Hydrargyrum
Antimony	Sb	Stibium
Tin	Sn	Stannum
Lead	Pb	Plumbum

Chemical Symbols for Elements

So far, scientists have discovered 90 naturally occurring elements and have made 28 more, for a total of 118. Each element is assigned a unique **chemical symbol**, which can be used as an abbreviation for the name of the element. Chemical symbols are also used to stand for atoms of elements when we write *chemical formulas* such as H_2O (water) and CO_2 (carbon dioxide). We will have a lot more to say about formulas later.

The names and chemical symbols of the elements are given on the inside front cover of the book. In most cases, an element's chemical symbol is formed from one or two letters of its English name. For instance, the symbol for carbon is C, for bromine it is Br, and for silicon it is Si. For some elements, the symbols are derived from their non-English names. Those that come from their Latin names, given to them long ago, are listed in Table 1.2. The symbol for tungsten (W) comes from *wolfram*, the German name of the element. Regardless of the origin of the symbol, the first letter is always capitalized and the second letter, if there is one, is always lowercase.

Figure 1.4 | **Mixtures can have variable compositions.** Orange juice, Coca-Cola, and pancake syrup are mixtures that contain sugar. The amount of sugar varies from one to another because the composition can vary from one mixture to another. *(Thomas Brase/Stone/Getty Images; Andy Washnik; Andy Washnik)*

Compounds

By means of chemical reactions, elements combine in various *specific proportions* to give all of the more complex substances in nature. Thus, hydrogen and oxygen combine to form water (H_2O), and sodium and chlorine combine to form sodium chloride (NaCl, common table salt). Water and sodium chloride are examples of compounds. A **compound** is a substance formed from two or more *different elements* in which the elements are always combined in the same, fixed (i.e., constant) proportions by mass. For example, if any sample of pure water is decomposed, the mass of oxygen obtained is *always* eight times the mass of hydrogen. Similarly, when hydrogen and oxygen react to form water, the mass of oxygen consumed is always eight times the mass of hydrogen, never more and never less.

Mixtures

Elements and compounds are examples of **pure substances.**[3] The composition of a pure substance is always the same, regardless of its source. Pure substances are rare, however. Usually, we encounter mixtures of compounds or elements. Unlike elements and compounds, **mixtures** *can have variable compositions.* For example, Figure 1.4 shows three mixtures that contain sugar. They have different degrees of sweetness because the amount of sugar in a given size sample varies from one to the other.

Mixtures can be either homogeneous or heterogeneous. A **homogeneous mixture** has the same properties throughout the sample. An example is a thoroughly stirred mixture of sugar in water. We call such a homogeneous mixture a **solution.** Solutions need not be liquids, just homogeneous. For example, the alloy used in the U.S. 5 cent coin is a solid solution of copper and nickel, and clean air is a gaseous solution of oxygen, nitrogen, and a number of other gases.

A **heterogeneous mixture** consists of two or more regions, called **phases,** that differ in properties. A mixture of olive oil and vinegar in a salad dressing, for example, is a two-phase mixture in which the oil floats on the vinegar as a separate layer (Figure 1.5). The phases in a mixture don't have to be chemically different substances like oil and vinegar, however. A mixture of ice and liquid water is a two-phase heterogeneous mixture in which the phases have the same chemical composition but occur in different *physical states* (a term we discuss further in Chapter 2).

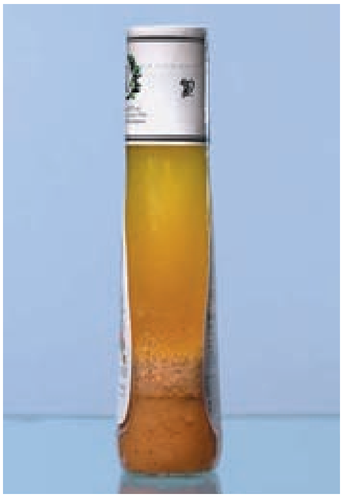

Figure 1.5 | **A heterogeneous mixture.** The salad dressing shown here contains vinegar and vegetable oil (plus assorted other flavorings). Vinegar and oil do not dissolve in each other, and they form two layers. The mixture is heterogeneous because each of the separate phases (oil, vinegar, and other solids) has its own set of properties that differ from the properties of the other phases.
(Andy Washnik)

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[3] We have used the term *substance* rather loosely until now. Strictly speaking, **substance** really means *pure substance*. Each unique chemical element and compound is a *substance*; a mixture consists of two or more substances.

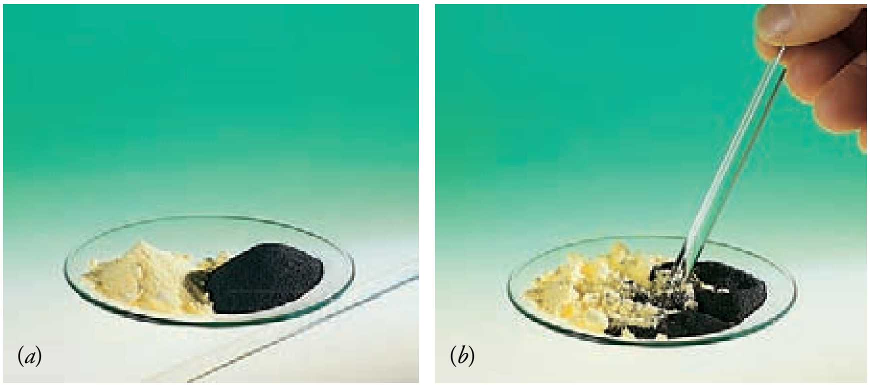


Figure 1.6 | **Formation of a mixture of iron and sulfur.** (*a*) Samples of powdered sulfur and powdered iron. (*b*) A mixture of sulfur and iron is made by stirring the two powders together. *(Michael Watson)*

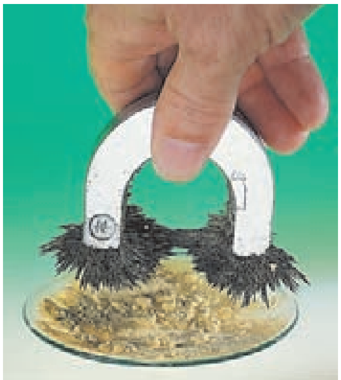


Figure 1.7 | **Formation of a mixture does not change chemical composition.** Here we see that forming the mixture has not changed the iron and sulfur into a compound of these two elements. The mixture can be separated by pulling the iron out with a magnet. Making a mixture involves a physical change. *(Michael Watson)*

Physical and Chemical Changes

The process we use to create a mixture involves a **physical change,** because no new chemical substances form. This is illustrated in Figure 1.6 for powdered samples of the elements iron and sulfur. By simply dumping them together and stirring, the mixture forms, but both elements retain their original properties. To separate the mixture, we could similarly use just physical changes. For example, we could remove the iron by stirring the mixture with a magnet — a physical operation. The iron powder sticks to the magnet as we pull it out, leaving the sulfur behind (Figure 1.7). The mixture also could be separated by treating it with a liquid called carbon disulfide, which is able to dissolve the sulfur but not the iron. Filtering the sulfur solution from the solid iron, followed by evaporation of the liquid carbon disulfide from the sulfur solution, gives the original components, iron and sulfur, separated from each other.

The formation of a compound involves a **chemical change** (a chemical reaction) because the chemical makeup of the substances involved are changed. Iron and sulfur, for example, combine to form a compound often called "fool's gold" because it looks so much like real gold (Figure 1.8). In this compound the elements no longer have the same properties they had before they combined, and they cannot be separated by physical means. The decomposition of fool's gold into iron and sulfur is also a chemical reaction.

The relationships among elements, compounds, and mixtures are shown in Figure 1.9.

Figure 1.8 | **"Fools gold."** The mineral pyrite (also called iron pyrite) is a compound of iron and sulfur. When the compound forms, the properties of iron and sulfur disappear and are replaced by the properties of the compound. Pyrite has an appearance that caused some miners to mistake it for real gold. *(WILDLIFE/Peter Arnold, Inc.)*

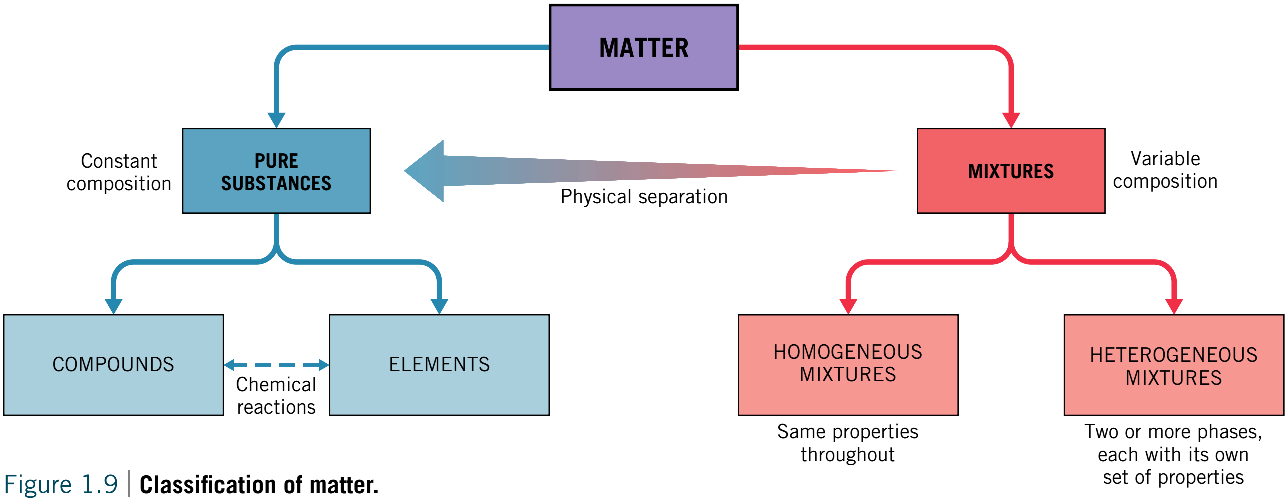

MATTER
Constant composition
PURE SUBSTANCES
Physical separation
MIXTURES
Variable composition
COMPOUNDS
Chemical reactions
ELEMENTS
HOMOGENEOUS MIXTURES
Same properties throughout
HETEROGENEOUS MIXTURES
Two or more phases, each with its own set of properties

Figure 1.9 | **Classification of matter.**

1.4 | Dalton and the Atomic Theory

In our definition of an element in Section 1.3, no reference was made to the atomic nature of matter. In fact, the distinction between elements and compounds had been made even before the atomic theory of matter was formulated. In this section we examine how the atomic theory began. This will enable us to take a closer look at elements, compounds, and mixtures in terms of our modern view of atomic structure.

The concept of atoms began nearly 2500 years ago when certain Greek philosophers expressed the belief that matter is ultimately composed of tiny indivisible particles, and it is from the Greek word *atomos*, meaning "not cut," that the word *atom* is derived. The philosophers' conclusions, however, were not supported by any evidence; they were derived simply from philosophical reasoning. Scientific support for the existence of atoms awaited the establishment of the *law of definite proportions* and the *law of conservation of mass*—two important general observations about the nature of compounds and chemical reactions.

Laws of Chemical Combination

Prior to the nineteenth century, progress in science was slow because there was little understanding of the need for accurate measurements. Over the course of time, however, scientists gradually accumulated data that revealed some truths that apply to all chemical compounds and chemical reactions.

The first, which we've actually used in our definition of a compound, is that when a compound is formed, elements always combine in the same proportion by mass. For example, we noted that when hydrogen and oxygen combine to form water, the mass of oxygen that reacts is *always* eight times the mass of hydrogen—never more and never less. In forming water, we cannot alter this ratio no matter how hard we try. Similar observations apply to every compound we study. Such observations led to a generalization known as the **law of definite proportions** (or **law of definite composition**): *In any chemical compound the elements are always combined in a definite proportion by mass.*

The second observation is that when a reaction is carried out in a sealed vessel, so that nothing can escape or enter the reaction mixture, the total mass after the reaction is over is exactly the same as before the reaction began. For instance, if we place a certain mass of hydrogen, plus eight times that mass of oxygen, into a sealed container and initiate the reaction to form water, the mass of water after the reaction is over is the same as the masses of hydrogen and oxygen we started with. Such observations, repeated over and over for large numbers of chemical reactions, led to another generalization known as the **law of conservation of mass:** *Mass is neither lost nor created during a chemical reaction.*

Law of Definite Proportions

In a given chemical compound, the elements are always combined in the same proportions by mass.

Law of Conservation of Mass

No detectable gain or loss of mass occurs in chemical reactions. Mass is *conserved.*

TOOLS

Laws of definite proportions and conservation of mass

■ Important relationships that we will use in solving chemistry problems are identified by this Tools icon in the margin. In this case, the tools are two important chemical laws that affect how we write chemical formulas and chemical equations. How the tools are used is summarized on page 24.

In Chapter 2 you will see how these laws can be used to perform calculations related to chemical composition.

The Atomic Theory

The laws of definite proportions and conservation of mass served as the *experimental foundation* for the atomic theory. They prompted the question: "What must be true about the nature of matter, given the truth of these laws?" In other words, what is matter made of?

At the beginning of the nineteenth century, John Dalton (1766–1844), an English scientist, used the Greek concept of atoms to make sense out of the laws of definite proportions and conservation of mass. Dalton reasoned that if atoms really exist, they must have certain properties to account for these laws. He described what those properties must be, and the list constitutes what we now call **Dalton's atomic theory.**

Dalton's Atomic Theory

1. *Matter consists of tiny particles called atoms.*
2. *In any sample of a pure element, all the atoms are identical in mass and other properties.*
3. *The atoms of different elements differ in mass and other properties.*
4. *When atoms of different elements combine to form compounds, new and more complex particles form. However, in a given compound the constituent atoms are always present in the same fixed* ***numerical*** *ratio.*
5. *Atoms are indestructible. In chemical reactions, the atoms rearrange but they do not themselves break apart.*

Modern Experimental Evidence for Atoms

■ The Nobel Prize, consisting of a gold medal, a citation, and a sum of money, was established in 1895 by the Swedish chemist Alfred Bernhard Nobel, the inventor of dynamite. It was first awarded for physics, chemistry, physiology or medicine, literature, and peace in 1901.

In Section 1.5 we will study how Dalton's theory accounted for the laws of definite proportions and conservation of mass. Before we get to this, however, you might wonder whether there is any additional proof today that atoms actually exist. Although atoms and most molecules are so incredibly tiny that even the most powerful optical microscopes are unable to detect them, experiments have been performed that provide pretty convincing evidence that atoms are real.

In recent times, scientists have developed very sensitive instruments that are able to map the surfaces of solids with remarkable resolution. One such instrument is called a **scanning tunneling microscope.** It was invented in the early 1980s by Gerd Binnig and Heinrich Rohrer and earned them the 1986 Nobel Prize in physics. With this instrument, the tip of a sharp metal probe is brought very close to an electrically conducting surface and an electric current bridging the gap is begun. The flow of current is extremely sensitive to the distance between the tip of the probe and the sample. As the tip is moved across the surface, the height of the tip is continually adjusted to keep the current flow constant. By accurately recording the height fluctuations of the tip, a map of the hills and valleys on the surface is obtained. The data are processed using a computer to reveal an image of atoms on the surface. (See Figure 1.10.)

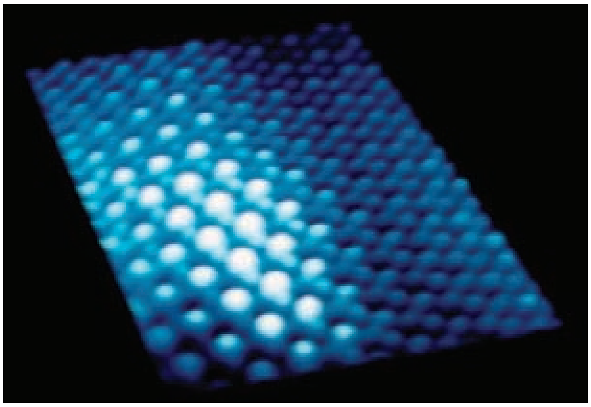


Figure 1.10 | **Individual atoms can be imaged using a scanning tunneling microscope.** This STM micrograph reveals the pattern of individual atoms of palladium deposited on a graphite surface. Palladium is a silvery white metal used in alloys such as white gold and dental crowns. *(P. Plailly/Phototake)*

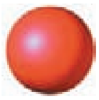
1.5 | Atoms and Molecules and Chemical Formulas

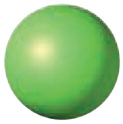
TOOLS

Colors used to represent atoms

In describing substances at the atomic level, it is frequently useful to use mental or graphic images of the way the individual atoms combine. Because we live in a three-dimensional world, atoms are represented as spheres (circles if you're drawing them by hand). Different colors are used to differentiate atoms of one element from those of another. In most of the artwork in this book, the standard color scheme shown in Figure 1.11 will be followed. Scientists are not locked into this color scheme, however, and sometimes colors are chosen to emphasize some particular aspect of a substance. In such cases, the legend for the figure will identify which colors are associated with which elements. You should learn to recognize atoms in drawings according to their colors.

Atoms of different elements have different sizes, so often the size of the sphere used to represent an atom will be large for larger atoms and small for smaller atoms. This is done when we particularly wish to emphasize size difference among atoms. The sizes of the different spheres in Figure 1.11 roughly indicate the relative sizes of the atoms. The following illustrate the relative sizes of atoms of oxygen and chlorine. As suggested by these drawings, a chlorine atom is larger than an oxygen atom.


oxygen atom
O


chlorine atom
Cl

Earlier we mentioned that each element is assigned its own unique chemical symbol, which can be used as shorthand for the name of the element or to represent a single atom of the element. Thus an atom of oxygen is represented by the symbol O and an atom of chlorine by the symbol Cl.

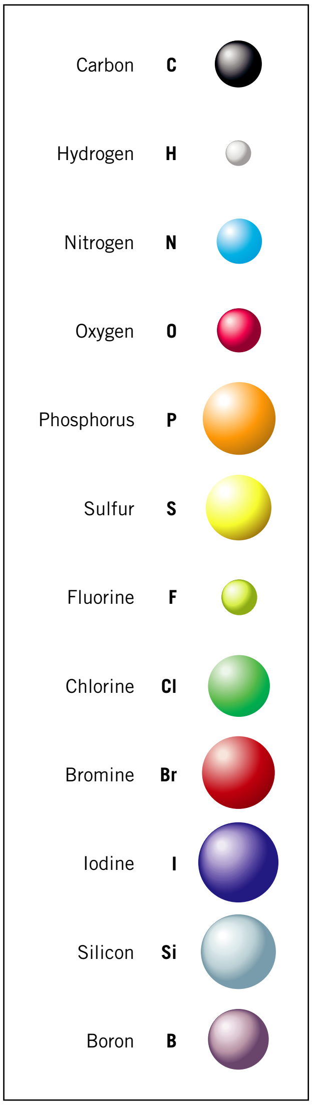


Figure 1.11 | **Colors used to represent atoms of different elements.** The sizes of the spheres roughly illustrate the relative sizes of the different atoms. The atomic symbols of the elements are shown next to their names.

Molecules

Atoms combine in a variety of ways to form all of the more complex substances we find in nature. One type of substance consists of discrete particles called **molecules**, each of which is made up of two or more atoms. Enormous numbers of different compounds as well as many elements exist in nature as molecules.[4] Another type of compound (called an *ionic compound*) consists of electrically charged atoms and will be discussed in Chapter 3.

Chemical Formulas

To describe chemical substances, both elements and compounds, we commonly use **chemical formulas**, in which chemical symbols are used to represent atoms of the elements that are present. For a **free element** (one that is not combined with another element in a compound) we often simply use the chemical symbol. Thus, the element sodium is represented by its symbol, Na, which is interpreted to mean one atom of sodium.

Many of the elements we encounter frequently are found in nature as **diatomic molecules** (molecules composed of two atoms each). Among them are the gases hydrogen, oxygen, nitrogen, and chlorine. A **subscript** following the chemical symbol is used to indicate the number of atoms of an element in a molecule. Thus, the formula for molecular hydrogen is H_2, and those for oxygen, nitrogen, and chlorine are O_2, N_2, and Cl_2, respectively. Drawings of these molecules are shown in Figure 1.12. A more complete list of such elements is found in Table 1.3. This would be a good time to learn the formulas of these elements because you will come upon them often throughout the course.

Just as chemical symbols can be used as shorthand notations for the names of elements, a chemical formula is a shorthand way of writing the name for a compound. However, *the most important characteristic of a compound's formula is that it specifies the atomic composition of the substance.*

In the formula of a compound, each element present is identified by its chemical symbol. Water, H_2O, is probably the best known example and consists of two atoms of hydrogen and one of oxygen. The lack of a subscript after the symbol O means that the formula specifies just one atom of oxygen. Another example is methane, CH_4, the combustible compound found in "natural gas," which is used for cooking in the kitchen and Bunsen burners in the lab. The formula tells us that methane molecules are composed of one atom of carbon and four atoms of hydrogen.

TOOLS

Symbols and subscripts in a chemical formula

Table 1.3 **Elements That Occur Naturally as Diatomic Molecules**

Hydrogen	H_2	Fluorine	F_2
Nitrogen	N_2	Chlorine	Cl_2
Oxygen	O_2	Bromine	Br_2
		Iodine	I_2

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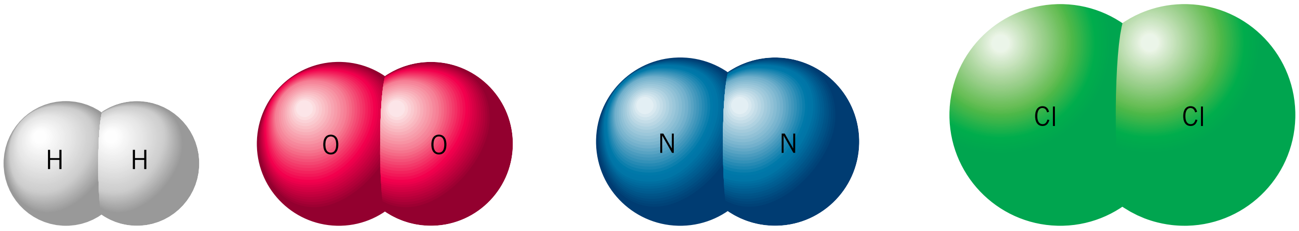
[4] CAS REGISTRY, the most comprehensive and high-quality compendium of publicly disclosed chemical information, now includes 50 million compounds!



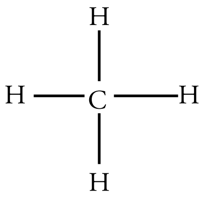
Hydrogen molecule, H_2 Oxygen molecule, O_2 Nitrogen molecule, N_2 Chlorine molecule, Cl_2

Figure 1.12 | **Models that depict the diatomic molecules of hydrogen, oxygen, nitrogen, and chlorine.** Each contains two atoms per molecule; their different sizes reflect differences in the sizes of the atoms that make up the molecules. The atoms are shaded by color to indicate the element (hydrogen, white; oxygen, red; nitrogen, blue; and chlorine, green).

■ Knowing the arrangement of atoms in a molecule is not something that is obvious from its chemical formula. We discuss some of this in later chapters.

When sufficient information is available it is possible to represent how the atoms in a molecule are connected to each other and even the three-dimensional shape of a molecule. To show how the atoms are connected, we can use chemical symbols to represent the atoms and dashes to indicate the *chemical bonds* that bind the atoms to each other. This kind of formula is often called a *structural formula*.

$H—O—H$



$$\begin{array}{ccc} & H & \\ & | & \\ H— & C & —H \\ & | & \\ & H & \end{array}$$

H_2O
water

CH_4
methane

■ Molecular model kits can be purchased that consist of balls with different colors corresponding to the different elements. Also supplied are sticks that can be used to connect the balls to form models of different molecules. The balls have holes drilled at specific angles to give the "molecules" their correct shapes.

■ *WileyPLUS*, found on the Web site for the text, has a number of interactive molecular visualizations that allow you to view and rotate molecules in three dimensions.

Later we will explore in depth the concept of chemical bonds, but for now we can just think of them as "connections" between atoms.

Three-dimensional representations of molecules can take several forms. One is called a **"ball-and-stick" model,** in which spheres representing atoms are connected by sticks that indicate the connections between the atoms. Ball-and-stick models of methane, CH_4 (natural gas), and chloroform, $CHCl_3$ (a compound once used as an anesthetic) are shown in Figure 1.13. Notice that the formula $CHCl_3$ describes a molecule in which there is one atom each of carbon and hydrogen as well as three atoms of chlorine.

Another type of representation is called a **"space-filling" model,** which shows the relative sizes of the atoms and how they take up space with the molecule. The drawings of the diatomic molecules in Figure 1.12 are examples. Space-filling models for water, methane, and chloroform molecules are shown in Figure 1.14.

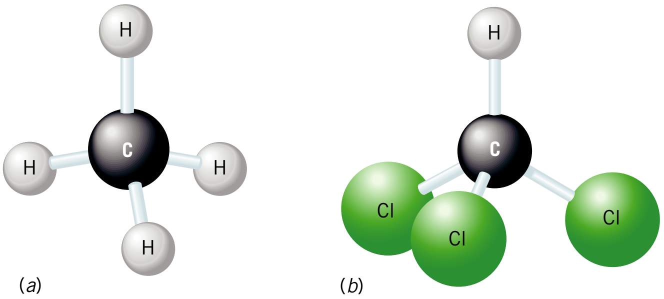


Figure 1.13 | **Ball-and-stick models.** (*a*) Methane, CH_4. (*b*) Chloroform, $CHCl_3$.

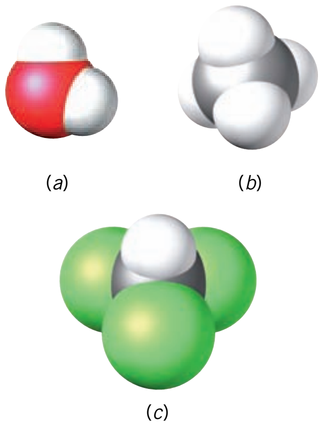

(*a*) (*b*) (*c*)

Figure 1.14 | **Space-filling models.** (*a*) Water, H_2O. (*b*) Methane, CH_4. (*c*) Chloroform, $CHCl_3$.

For more complicated compounds, we sometimes find formulas that contain parentheses. An example is the formula for urea, $CO(NH_2)_2$, which tells us that the group of atoms within the parentheses, NH_2, occurs twice. (The formula for urea could also be written as CON_2H_4, but there are good reasons for writing certain formulas with parentheses, as you will see later.) Ball-and-stick and space-filling models of urea are shown in Figure 1.15.

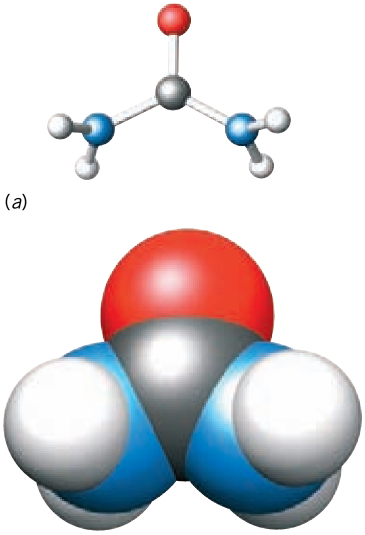

(*a*) (*b*)

Figure 1.15 | **Models of the urea molecule, $CO(NH_2)_2$.** (*a*) Ball-and-stick model. (*b*) Space-filling model.

Hydrates: Crystals That Contain Water in Fixed Proportions

Certain compounds form crystals that contain water molecules. An example is ordinary plaster — the material often used to coat the interior walls of buildings. Plaster consists of crystals of a compound called calcium sulfate, $CaSO_4$, which contain two molecules of water for each $CaSO_4$. These water molecules are not held very tightly and can be driven off by heating the crystals. The dried crystals absorb water again if exposed to moisture, and the amount of water absorbed always gives crystals in which the H_2O-to-$CaSO_4$ ratio is 2 to 1. Compounds whose crystals contain water molecules in fixed ratios are called **hydrates,** and they are quite common. The formula for this hydrate of calcium sulfate is written $CaSO_4 \cdot 2H_2O$ to show that there are two molecules of water per $CaSO_4$. The raised dot is used to indicate that the water molecules are not bound very tightly in the crystal and can be removed.

Sometimes the *dehydration* (removal of water) of hydrate crystals produces changes in color. An example is copper sulfate, which is sometimes used as an agricultural fungicide. Copper sulfate forms blue crystals with the formula $CuSO_4 \cdot 5H_2O$ in which there are five water molecules for each $CuSO_4$. When the blue crystals are heated, most of the water is driven off and the solid that remains, now nearly pure $CuSO_4$, is almost white (Figure 1.16). If left exposed to the air, the $CuSO_4$ will absorb moisture and form blue $CuSO_4 \cdot 5H_2O$ again.

■ When all the water is removed, the solid is said to be **anhydrous**, meaning without water.

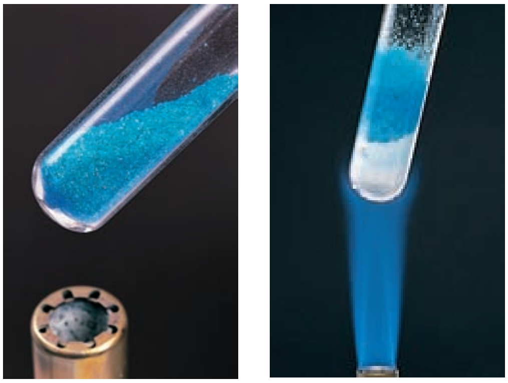

(*a*) (*b*)

Figure 1.16 | **Water can be driven from hydrates by heating.** (*a*) Blue crystals of copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, about to be heated. (*b*) The hydrate readily loses water when heated. The light-colored solid observed in the lower half of the test tube is pure $CuSO_4$. *(Richard Megna/Fundamental Photographs; Michael Watson)*

Counting Atoms in Formulas: A Necessary Skill

Counting the number of atoms of the elements in a chemical formula is an operation you will have to perform many times, so let's look at an example.

■ An Important Word about Problem Solving

Learning chemistry is far more than memorizing facts and formulas. To a large degree, your success in this course will be tied to your ability to solve problems, both numerical and non-numerical. Because this is so important, one of the principal goals of this textbook is to help you develop and improve your problem-solving skills. Toward this end we include a large number of detailed worked examples throughout the book. You should study these and then work the similar practice exercises that follow. The answers to all of the practice exercises are in Appendix B at the back of the book, so you can check your work as you proceed.

You will find each of the examples divided into four steps intended to guide you through the thought processes followed by good problem solvers. We encourage you to practice this approach when you tackle problems on your own. As you gain experience, these steps will merge into a seamless, effective way to solve problems, not only in chemistry but in other subjects as well. Let's take a brief look at these four steps and the purpose of each.

■ **Analysis:** If you intend to drive from your home to someplace you haven't been before, you don't just jump in the car and start driving. You first give some thought to where you're going and the route you have to take. Solving chemistry problems begins the same way. In the *Analysis* section, we identify exactly what is being asked and then plan what we have to do to arrive at the solution. Sometimes the analysis will be relatively simple, but with more complex problems, you may have to spend some time thinking about how to solve the problem. You may find it necessary to review a concept to be certain you're on the right track.

■ **Assembling the Tools:** After we've determined how to proceed, the next step is to assemble the various *chemical tools* that apply to the particular problem at hand. These are the tools that have been developed in the text and are identified by the "Tool" icon in the margin. Each tool is chosen because it accomplishes a task required to solve the problem.

■ **Solution:** At last we're ready to work out the answer by applying the appropriate tool to each step of the plan we developed in the *Analysis* section. This is really the simplest part of the problem, because we've already figured out what we have to do and which tools we need to do the job.

■ **Is the Answer Reasonable?** The preceding step has given us an answer, but is it the right answer? Does the answer make sense? It is always prudent to conclude your problem-solving experience with a quick check to see whether the answer is reasonable. As we progress, you will learn some techniques to help you check your answer.

In solving a problem, you have to be flexible. There may be times when you're able to figure out part of a problem in the *Analysis* step, but the full solution isn't apparent. If this happens, proceed with the next two steps and then come back to the *Analysis* again to try to plan the rest of the solution.

The most important thing to remember in working problems in this book is that all of the concepts and tools necessary to solve them have been given to you. If you're struggling, don't despair. Take a break and come back with a fresh perspective. You can be successful.

Example 1.1
Counting Atoms in Formulas

How many atoms of each element are represented by the formulas (a) $(CH_3)_3COH$ and (b) $CoCl_2{\cdot}6H_2O$? In each case, identify the elements in the compound by name.

Analysis: This is not a difficult problem, but let's proceed methodically just for practice. To answer both parts of this question requires that we understand the meaning of subscripts and parentheses in formulas. We also have to make a connection between the chemical symbol and name of the element, so we need to know where to find this information if we don't already know it.

Assembling the Tools: Here are the three tools we will use: (1) The subscript following a symbol indicates how many of that element are part of the formula; a subscript of 1 is implied if there is no subscript. (2) A quantity within parentheses is repeated a number of times equal to the subscript that follows. (3) A raised dot in a formula indicates the substance is a hydrate in which the number preceding H_2O specifies how many water molecules are present.

You will gradually learn the names and symbols for many elements. If you forget, you can refer to the table inside the front cover of the book.

Solution: (a) Here we must recognize that all the atoms within the parentheses occur three times.

Subscript 3 indicates three CH_3 units

$$(CH_3)_3COH$$

Each CH_3 contains one C and three H atoms, so three of them contain three C and nine H atoms. In the COH unit, there is one additional C and one additional H, which gives a total of four C atoms and 10 H atoms. The molecule also contains one O atom. Therefore, the formula $(CH_3)_3COH$ shows

4 C   10 H   1 O

The elements in the compound are carbon (C), hydrogen (H), and oxygen (O).

(b) This is a formula for a hydrate, as indicated by the raised dot. It contains six water molecules, each with two H and one O, for every $CoCl_2$.

The 6 indicates there are 6 molecules of H_2O.

$$CoCl_2{\cdot}6H_2O$$

The dot indicates the compound is a hydrate.

Therefore, the formula $CoCl_2{\cdot}6H_2O$ represents

1 Co   2 Cl   12 H   6 O

Checking the table inside the front cover of the book, we see that the elements here are cobalt (Co), chlorine (Cl), hydrogen (H), and oxygen (O).

Are the Answers Reasonable? The only way to check the answer here is to perform a recount.

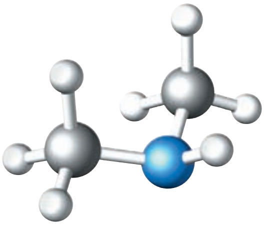
Practice Exercises[5]

1.1 | How many atoms of each element are expressed by the following formulas? (*Hint:* Pay special attention to counting elements within parentheses.)

(a) SF_6 (b) $(C_2H_5)_2N_2H_2$ (c) $Ca_3(PO_4)_2$ (d) $Co(NO_3)_2{\cdot}6H_2O$

1.2 | How many atoms of each element are present in each of the formulas below? Consult the table inside the front cover to write the full name of each element as well as its symbol.

(a) NH_4NO_3 (b) $FeNH_4(SO_4)_2$ (c) $Mo(NO_3)_2{\cdot}5H_2O$ (d) $C_6H_4ClNO_2$



1.3 | Write the chemical formula for the fishy-smelling compound with the molecular structure shown in the margin. (See Figure 1.11.) There are groups of atoms that can be written as CH_3 in this molecule. Rewrite the chemical formula for the compound to show the presence of these CH_3 groups.

Atoms, Molecules, and the Law of Definite Proportions

Let's now use our methods of representing atoms and molecules to understand how Dalton's atomic theory accounts for the law of definite proportions. According to the theory, all of the molecules of a compound are alike and contain atoms in the same numerical ratio. Thus all water molecules have the formula H_2O and contain two atoms of hydrogen and one of oxygen.

Today we know that oxygen atoms are much heavier than hydrogen atoms. In fact, one oxygen atom weighs 16 times as much as a hydrogen atom. We haven't said how much mass this is, so let's say that one hydrogen atom has a mass of one unit. On this scale an oxygen atom would then weigh 16 times as much, or 16 mass units.

1 H atom	1 mass unit
1 O atom	16 mass units

In Figure 1.17*a* we see one water molecule with two hydrogen atoms and one oxygen atom. The mass of oxygen in that molecule (16 mass units) is eight times the total mass of hydrogen (2 mass units). In Figure 1.17*b* we have five water molecules containing a total of 10 hydrogen atoms and 5 oxygen atoms. Notice that the total mass of oxygen in the five molecules is, once again, eight times the total mass of hydrogen. Regardless of the number of water molecules in the sample, the total mass of oxygen is eight times the total mass of hydrogen.

Recall from Section 1.3 that in any sample of pure water, the mass of oxygen present is always found experimentally to be eight times the mass of hydrogen—an example of how the law of definite proportions applies to water. Figure 1.17 explains *why* the law works in terms of the atomic theory.

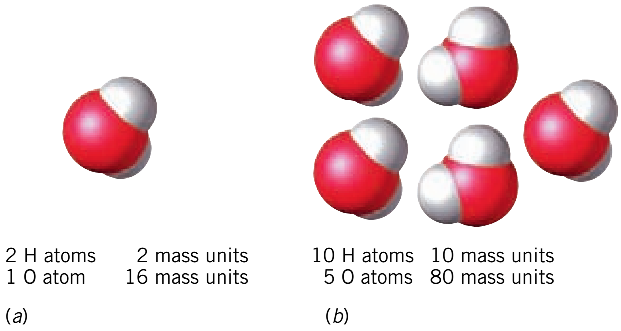


Figure 1.17 | **Law of Definite Proportions.** Regardless of the number of water molecules, the mass of oxygen is always eight times the mass of hydrogen.

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[5] Answers to the Practice Exercises are found in Appendix B at the back of the book.

The Law of Multiple Proportions

One of the real successes of Dalton's atomic theory was that it predicted another chemical law—one that had not been discovered yet. This law is called the law of multiple proportions and applies to atoms that are able to form two or more different compounds with each other.

> **Law of Multiple Proportions**
>
> Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

To see what this means, consider the two compounds sulfur dioxide, SO_2, and sulfur trioxide, SO_3, which are illustrated in Figure 1.18. In one molecule of each of these compounds there is one atom of sulfur, so both molecules must have the *same mass of sulfur*. Now let's focus on the oxygen. The SO_2 molecule has two O atoms; the SO_3 molecule has three O atoms. This means that the ratio of the atoms of O in the two compounds is 2-to-3.

$$\frac{\text{atoms of O in SO}_2}{\text{atoms of O in SO}_3} = \frac{2 \text{ atoms O}}{3 \text{ atoms O}} = \frac{2}{3}$$

Because all O atoms have the same mass, the *ratio* of the masses of O in the two molecules *must* be the same as the ratio of the atoms, and this ratio (2/3) is a ratio of small whole numbers.

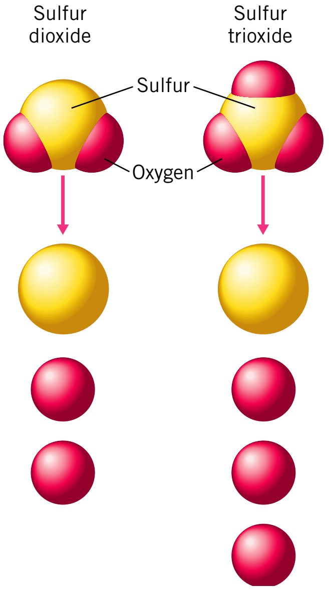


Figure 1.18 | **Oxygen compounds of sulfur demonstrate the law of multiple proportions.** Illustrated here are molecules of sulfur trioxide and sulfur dioxide. Each has one sulfur atom, and therefore the same mass of sulfur. The oxygen ratio is 2-to-3, both by atoms and by mass.

Molecules Small and Large

All of the molecules we've discussed so far are considered to be small molecules because there are so few atoms in each of them. Most of the molecules you will encounter in this book would generally be considered to be small. However, nature does present us with some very large molecules as well, particularly in living organisms. For example, DNA, which is the molecule that differentiates humans from all other species of living things on the planet, consists of millions of atoms woven into a very complex structure. A short segment of a DNA molecule is illustrated in Figure 1.19. We will say more about DNA in Chapter 23.

■ DNA, which stands for *deoxyribonucleic acid,* carries the instructions a cell uses to manufacture molecules needed for it to function.

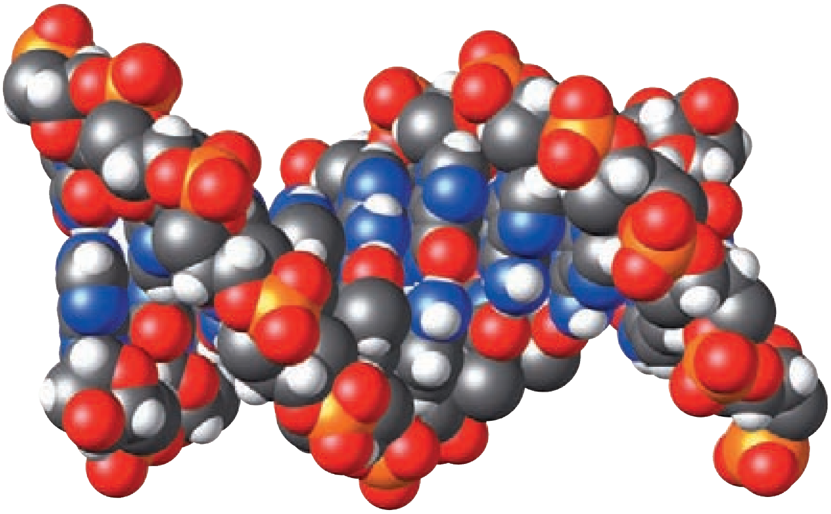


Figure 1.19 | **Some molecules are extremely large.** Shown here is a short segment of a DNA molecule, the structure of which is responsible for the diffences between the various species of living things on earth. An entire DNA molecule contains millions of atoms.

ON THE CUTTING EDGE 1.1

Nanotechnology: Controlling Structure at the Molecular Level

Atoms and small molecules are incredibly tiny. Experiments have shown that they have diameters of the order of several billionths of an inch. For example, the diameter of a carbon atom is about 6 billionths of an inch (6×10^{-9} in.). As you will learn in Chapter 2, the prefix *nano* implies 10^{-9}, so when we examine matter at the *nano-scale* level, we are looking at very small structures, usually with dimensions of perhaps tens to hundreds of atoms. **Nanotechnology** deals with using such small-scale objects and the special properties that accompany them to develop useful applications. Ultimately, the goal of nanotechnology (also sometimes called **molecular nanotechnology**) is to be able to build materials from the atom up. Such technology doesn't quite exist yet, but scientists are beginning to make progress in that direction. This discussion, therefore, is kind of a progress report that will give you some feeling of where science is now and where it's heading—sort of a glimpse at the future.

There are several reasons why there is so much interest in nanotechnology. For one, the properties of materials are related to their structures. By controlling structures at the atomic and molecular level, we can (in principle) tailor materials to have specific properties. Driving much of the research in this area is the continuing efforts by computer and electronics designers to produce ever smaller circuits. The reductions in size achieved through traditional methods are near their limit, so new ways to achieve smaller circuits and smaller electrical devices are being sought.

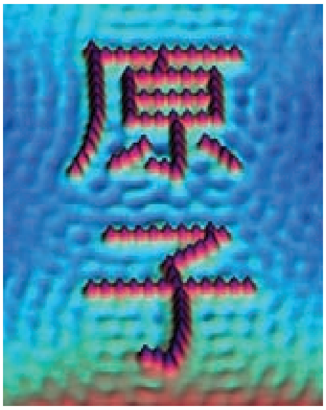
Molecular Self-Assembly

An area of research that is of great interest today is the field of molecular self-assembly, in which certain molecules, when brought together, spontaneously arrange themselves into desirable structures. Biological systems employ this strategy in constructing structures such as cellular membranes. The goal of scientists is to mimic biology by designing molecules that will self-assemble into specific arrangements.

Visualizing and Manipulating Very Tiny Structures

What has enabled scientists to begin the exploration of the nanoworld is the development of tools that allow them to see and sometimes manipulate individual atoms and molecules. We've already discussed one of these important devices, the scanning tunneling microscope (STM), when we discussed experimental evidence for atoms (see page 10). This instrument, which can only be used with electrically conducting samples, makes it possible to image individual atoms. What is very interesting is that it can also be used to move atoms around on a surface. To illustrate this, scientists have arranged atoms to spell out words (Figure 1). Although writing words with atoms doesn't have much practical use, it demonstrates that one of the required capabilities for working with substances at the molecular level is achievable.

Figure 1 **Atoms of iron on copper.** Scientists at IBM used an STM instrument to manipulate iron atoms into the Kanji letters for "atom." The literal translation is something like "original child." *(Courtesy IBM Research Division)*



To study nonconducting samples, a device called an **atomic force microscope (AFM)** can be used. Figure 2 illustrates its basic principles. A very sharp stylus (sort of like an old fashioned phonograph needle) is moved across the surface of the sample under study. Forces between the tip of the probe and the surface molecules cause the probe to flex as it follows the ups and downs of the bumps that are the individual molecules and atoms. A mirrored surface attached to the probe reflects a laser beam at angles proportional to the amount of deflection of the probe. A sensor picks up the signal from the laser and translates it into data that can be analyzed by a computer to give three-dimensional images of the sample's surface. A typical image produced by an AFM is shown in Figure 3.

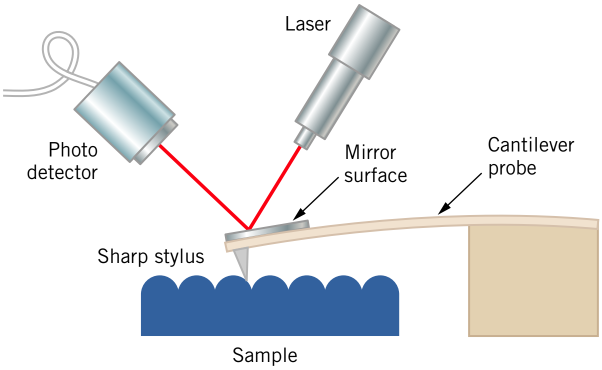


Figure 2 **An Atomic Force Microscope (AFM).** A sharp stylus attached to the end of a cantilever probe rides up and down over the surface features of the sample. A laser beam, reflected off a mirrored surface at the end of the probe, changes angle as the probe moves up and down. A photo detector reads these changes and sends the information to a computer, which translates the data into an image.

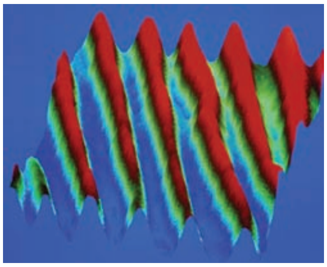


Figure 3 **Silver nanowires imaged using an atomic force microscope.** Colored micrograph of thin silver nanowires spaced about 0.8 millionth of an inch apart on a calcium fluoride crystal surface. Such wires could be used for miniature electronics. *(Science/Photo Library/Photo Researchers)*

The Relationship between Atoms, Molecules, and the World We See

At this point you may begin to think that the formulas and shapes of molecules come to chemists mysteriously "out of the blue." This is hardly the case. When a chemical is first prepared or isolated from nature, its formula is unknown. The compound, for example, might be produced from an experiment in the form of a white powder, and there's nothing about its formula or the arrangement of the atoms within it that come from the outward appearance of the substance. To acquire such knowledge chemists perform experiments, some of which will be described later in this book, that enable them to calculate what the formula of the substance is. Once a formula is known, we might speculate on the shape of the molecule, but a lot of work and very expensive and sophisticated instruments are required to know for sure. (If you take advanced courses in chemistry, it is likely you will get hands-on experience using such instruments.) It is important for you to understand that when we describe the formulas of compounds and the structures of molecules, such information is the culmination of the work of many scientists over many years.

Mixtures at the Atomic/Molecular Level

Earlier we noted that mixtures differ from elements and compounds in that mixtures can have variable compositions. Figure 1.20 illustrates this at the atomic/molecular level, where we have used different-color spheres to stand for two substances in a homogeneous mixture (also called a solution). Notice that the two substances are quite uniformly mixed. The difference between homogeneous and heterogeneous mixtures on the molecular level can be seen by comparing Figure 1.20 and 1.21.

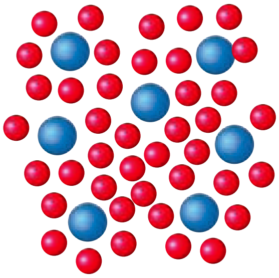


Figure 1.20 | **A portion of a homogeneous mixture viewed at the atomic/molecular level.** Red and blue spheres represent two different substances (not two different elements). One substance is uniformly distributed throughout the other.

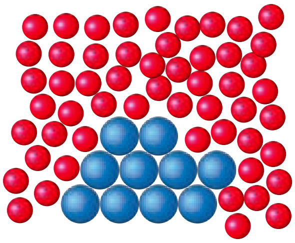


Figure 1.21 | **A portion of a heterogeneous mixture viewed at the atomic/molecular level.** Two substances exist in separate phases in a heterogeneous mixture.

1.6 | Chemical Reactions and Chemical Equations

Chemical reactions are at the heart of chemistry. When they occur, dramatic changes often occur among the chemicals involved. While chemical reactions are interesting to observe in the laboratory, they have an enormous number of applications in industry and ordinary everyday living. Some reactions occur rapidly and violently, such as the reaction between hydrogen and oxygen in the main engine of the space shuttle, which is used to help lift the vehicle from its launch pad (Figure 1.22). In this case, the reaction forms harmless water vapor. Other reactions are less violent. For example, you may use Clorox as a bleach because its active ingredients react with stains in clothing and also destroy bacteria. These are just two examples; many others lie in the pages ahead.

Figure 1.22 | **Reaction of hydrogen with oxygen.** This photo shows the three main engines of the space shuttle at full power an instant before the booster rockets fire and lift the space craft from its launch pad. The violent reaction of hydrogen with oxygen provides the thrust produced by the main engines. *(Courtesy NASA)*

Figure 1.23 | **The combustion of methane.** Gas-burning stoves that use natural gas (methane) as a fuel are common in many parts of the United States. The reaction consumes oxygen and produces carbon dioxide and water vapor. *(photocuisine/© Corbis)*

To understand chemical reactions, we need to observe how they lead to changes among the properties of chemical substances. Consider, for example, the mixture of elements iron and sulfur shown in Figure 1.6 on page 8. The sulfur has a bright yellow color, and the iron appears in this mixture as a black powder with magnetic properties. If these elements react, they can form a compound called iron sulfide (also known as "fools gold"), and as shown in Figure 1.8, it doesn't look like either sulfur or iron, and it is not magnetic. When iron and sulfur combine chemically, the properties of the elements give way to the new properties of the compound.

To see how a chemical change occurs at the atomic level, let's study the combustion of methane, CH_4, the chief component in natural gas used in typical gas-burning kitchen stoves (Figure 1.23). The reaction consumes CH_4 and oxygen (O_2, which is how oxygen occurs in nature) and forms in their place carbon dioxide, CO_2, and water, H_2O. Figure 1.24 illustrates the reaction at the atomic/molecular level. For the reaction between methane and oxygen, CH_4 and O_2 are the **reactants**; these are the substances present before the reaction begins and are shown on the left in Figure 1.24. On the right we see the **products** of the reaction, which are the molecules present after the reaction is complete. The arrow indicates that the reactants undergo the change to form the products.

Drawing pictures to describe a chemical change can be awkward. Instead, chemists normally use chemical symbols to describe reactions by writing chemical equations. A **chemical equation** uses chemical formulas to describe what happens when a chemical reaction occurs. As also shown in Figure 1.24, it describes the before-and-after picture of the chemical substances involved.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{1}$$

TOOLS

Coefficients in an equation

■ The coefficients of CH_4 and CO_2 are each equal to 1.

The symbols stand for atoms of the elements involved. The numbers that precede O_2 and H_2O are called **coefficients**. In this equation, the coefficients tell us how many CH_4 and O_2 molecules react and how many CO_2 and H_2O molecules are formed. Note that when no coefficient is written in front of a formula, it is assumed to be equal to 1. The arrow in a chemical equation is read as "reacts to yield." Thus, this chemical equation would be read as *methane and oxygen react to yield carbon dioxide and water.*

Chemical Reactions and Conservation of Mass

The law of conservation of mass says that mass is neither created nor destroyed in a chemical reaction. In Figure 1.24, observe that before the reaction begins there are four H atoms, four O atoms, and one C atom among the reactants. They are found in one CH_4 molecule and two O_2 molecules. After the reaction is over, we still have the same number of atoms of each kind, but they have become rearranged into one CO_2 molecule and two H_2O molecules. Because atoms are neither lost nor created during the reaction, the total mass must remain the same. Thus, by applying the concept of atoms and the postulate of Dalton's atomic theory that says atoms simply rearrange during a chemical reaction, we've accounted for the law of conservation of mass.

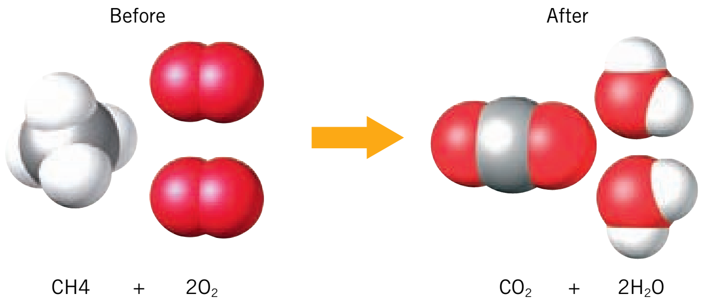


Figure 1.24 | **The reaction of methane, CH_4, with oxygen, O_2 to give carbon dioxide, CO_2, and water, viewed at the atomic-molecular level.** On the left are methane and oxygen molecules before reaction, and on the right are the carbon dioxide and water molecules that are present after the reaction is complete. Below the drawings is the chemical equation for the reaction.

Coefficients in Equations and the Law of Conservation of Mass

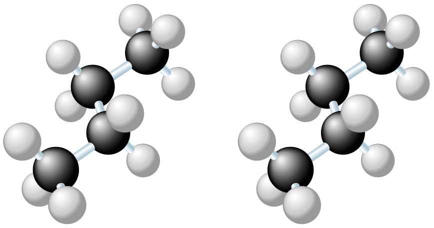
All chemical reactions obey the law of conservation of mass, which means that in any reaction the total number of atoms of each kind before and after are the same. When we write chemical equations we adjust the numbers of molecules on each side of the arrow to make the equation conform to this principle. We say we *balance* the equation, and we accomplish this by adjusting the coefficients in front of reactant and product molecules. In the equation for the combustion of methane, the coefficients in front of O_2 on the left and H_2O on the right make this a **balanced equation.**

Let's look at another example, the combustion of butane, C_4H_{10}, the fuel in disposable cigarette lighters (Figure 1.25).

Figure 1.25 | **The combustion of butane, C_4H_{10}.** The products are carbon dioxide and water vapor. *(Robert Capece)*

$$\underset{\text{Two molecules of } C_4H_{10}}{2C_4H_{10}} + \underset{\text{Thirteen molecules of } O_2}{13O_2} \longrightarrow \underset{\text{Eight molecules of } CO_2}{8CO_2} + \underset{\text{Ten molecules of } H_2O}{10H_2O}$$

The 2 before the C_4H_{10} tells us that two molecules of butane react. This involves a total of 8 carbon atoms and 20 hydrogen atoms, as we see in Figure 1.26. Notice that we



Two molecules of butane contain
8 atoms of C and 20 atoms of H.

Figure 1.26 | **Understanding coefficients in an equation.** The expression $2C_4H_{10}$ describes two molecules of butane, each of which contains 4 carbon and 10 hydrogen atoms. This gives a total of 8 carbon and 20 hydrogen atoms.

have multiplied the numbers of atoms of C and H in one molecule of C_4H_{10} by the coefficient 2. On the right we find 8 molecules of CO_2, which contain a total of 8 carbon atoms. Similarly, 10 water molecules contain 20 hydrogen atoms. Finally, there are 26 oxygen atoms on both sides of the equation. You will learn to balance equations such as this in Chapter 4. For now, however, you should be able to determine when an equation is balanced and when it is not.

Example 1.2
Determining Whether an Equation Is Balanced

Determine whether or not the following chemical equations are balanced. Support your conclusions by writing how many of each element is on either side of the arrow.

(a) $Fe(OH)_3 + 2HNO_3 \longrightarrow Fe(NO_3)_3 + 2H_2O$

(b) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

(c) $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

Analysis: The statement of the problem asks whether the equations are balanced. You can prove an equation is balanced if each element has the same number of atoms on either side of the arrow.

Assembling the Tools: The meaning of subscripts and parentheses in formulas as well as the meaning of coefficients in front of formulas are the tools we will use to count atoms. Note that in two of the equations, oxygen appears in both reactants and both products. We must be sure to count all of the atoms.

Solution:

(a) Reactants: 1 Fe, 9 O, 5 H, 2 N; Products: 1 Fe, 11 O, 4 H, 3 N Only Fe has the same number of atoms on either side of the arrow. This equation is *not* balanced.

(b) Reactants: 1 Ba, 2 Cl, 2 H, 1 S, 4 O; Products: 1 Ba, 2 Cl, 2 H, 1 S, 4 O. This equation *is* balanced.

(c) Reactants: 6 C, 12 H, 18 O; Products: 6 C, 12 H, 18 O. This equation *is* balanced.

Is the Answer Reasonable? The appropriate way to check this is to recount the atoms. Try counting the atoms in the reverse direction this time.

Practice Exercises

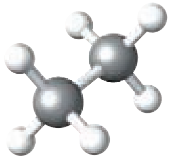
1.4 | How many atoms of each element appear on each side of the arrow in the following equation? (*Hint:* Recall that coefficients multiply the elements in the entire formula.)

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

1.5 | Count the number of atoms of each element on both sides of the arrow to determine whether the following equation is balanced.

$$2(NH_4)_3PO_4 + 3Ba(C_2H_3O_2)_2 \longrightarrow Ba_3(PO_4)_2 + 6NH_4C_2H_3O_2$$

1.6 | The gas ethane, C_2H_6, burns in oxygen (O_2) to give carbon dioxide (CO_2) and water. Use drawings to construct a balanced equation showing C_2H_6 and O_2 on the left and CO_2 and H_2O on the right. The ethane molecule can be represented as shown in the margin.



Summary

Chemistry and the Scientific Method. **Chemistry** is a science that studies the properties and composition of **matter**, which is defined as anything that has **mass** and occupies space. Chemistry employs the **scientific method** in which **observations** are used to collect **empirical facts**, or **data**, that can be summarized in **scientific laws**. **Models** of nature begin as **hypotheses** that mature into **theories** when they survive repeated testing.

Elements, Compounds, and Mixtures. An **element,** which is identified by its **chemical symbol**, cannot be decomposed into something simpler by a **chemical reaction**. Elements combine in fixed proportions to form **compounds**. Elements and compounds are **pure substances** that may be combined in *varying* proportions to give **mixtures**. If a mixture has two or more **phases**, it is **heterogeneous**. A one-phase **homogeneous** mixture is called a **solution**. Formation or separation of a mixture into its components can be accomplished by a **physical change**, which doesn't alter the chemical composition of the substances involved. Formation or decomposition of a compound takes place by a **chemical change** that changes the chemical makeup of the substances involved.

Atomic Theory. Dalton based his **atomic theory** on two laws of chemical combination, the **law of definite proportions** (in a compound, the elements are combined in fixed proportions by mass) and the **law of conservation of mass** (no change in mass occurs during a chemical reaction). Dalton's theory proposed that matter consists of indestructible **atoms** with masses that do not change during chemical reactions. During a chemical reaction, atoms may change partners, but they are neither created nor destroyed. After Dalton had proposed his theory, it was discovered that whenever two elements form more than one compound, the different masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers (the **law of multiple proportions**). Using modern instruments such as the **scanning tunneling microscope**, scientists are able to "see" atoms on the surfaces of solids.

Atoms, Molecules, and Chemical Formulas. In drawing atoms, spheres of different sizes and colors are used, each standing for a particular element. Each element has its own unique **chemical symbols**. Atoms combine to form more complex substances, many of which consist of **molecules** composed of two or more atoms.

Chemical formulas are used to describe chemical substances. **Subscripts** are used to indicate the number of atoms of each type in a molecule. Many common **free elements** occur as **diatomic molecules**. Chemical symbols can be used in drawings to indicate how atoms are attached to each other in compounds. Three-dimensional representations of molecules can be **ball-and-stick** or **space-filling models**. Some compounds form solids called **hydrates**, which contain water molecules in definite proportions.

Using atoms we can account for the law of definite proportions. The atomic theory also led to the discovery of the **law of multiple proportions.**

Chemical Reactions and Chemical Equations. Significant changes in the properties of substances are observed when **chemical reactions** occur, and **chemical equations** are used to show how the **reactants** change to **products**. **Coefficients** in front of formulas indicate the number of molecules that react or are formed and are used to balance an equation, making the total numbers of atoms of each kind the same on both sides of the arrow. A **balanced equation** conforms to the law of conservation of mass.

Tools for Problem Solving

In this chapter you learned a variety of concepts that are useful as tools for solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

Law of definite proportions (page 9)

When dealing with a chemical compound, we can rely on its formula to accurately describe its atomic composition in all samples of the substance. A given compound will *always* have the same atomic composition and the elements will always be present in the same proportions by mass.

Law of conservation of mass (page 9)

We use this law whenever we balance a chemical equation. When dealing with any chemical reaction, all of a given element in the reactants must also be present in the products. You will use this principle in chemical calculations in later chapters.

Colors used to represent different elements in a model of a molecule (page 11)

Use the color code in Figure 1.11 to recognize elements in a drawing of a model of a molecule.

Chemical symbols and subscripts in a chemical formula (page 11)

In a chemical formula, the chemical symbol stands for an atom of an element. Subscripts show the number of atoms of each kind represented in a chemical formula. When a subscript follows parentheses, it multiplies everything within the parentheses.

Coefficients in an equation (page 20)

Coefficients indicate the number of chemical units of each type that are present in reactants and products. They are used to balance an equation.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Introduction; the Scientific Method

1.1 After some thought, give two reasons why a course in chemistry will benefit *you* in the pursuit of your particular major.

1.2 What steps are involved in the scientific method?

1.3 What is the difference between (a) a law and a theory, (b) an observation and a conclusion, (c) an observation and data?

1.4 Can a theory be proved to be correct? Can a theory be proved to be wrong?

Properties of Substances

OH **1.5** Define *matter.* Which of the following are examples of matter? (a) air, (b) a pencil, (c) a cheese sandwich, (d) a squirrel, (e) your mother

1.6 What is *a physical change?* What is *a chemical change?* What is the chief distinction between physical and chemical changes?

1.7 "A sample of calcium (an electrically conducting white metal that is shiny, relatively soft, melts at 850 °C, and boils at 1440 °C) was placed into liquid water that was at 25 °C. The calcium reacted slowly with the water to give bubbles of gaseous hydrogen and a solution of the substance calcium hydroxide." Based on this description, what physical changes and what chemical changes occurred?

OH **1.8** In places like Saudi Arabia, freshwater is scarce and is recovered from seawater. When seawater is boiled, the water evaporates and the steam can be condensed to give pure water that people can drink. If all the water is evaporated, solid salt is left behind. Are the changes described here chemical or physical?

Elements, Compounds, and Mixtures

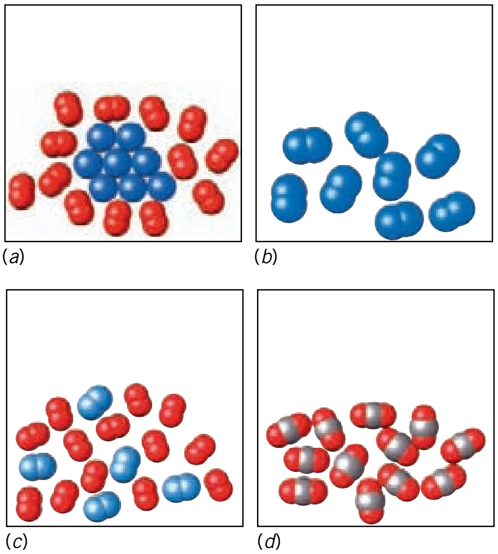
1.9 Define (a) element, (b) compound, (c) mixture, (d) homogeneous, (e) heterogeneous, (f) phase, (g) solution.

1.10 Which kind of change, chemical or physical, is needed to change a compound into its elements?

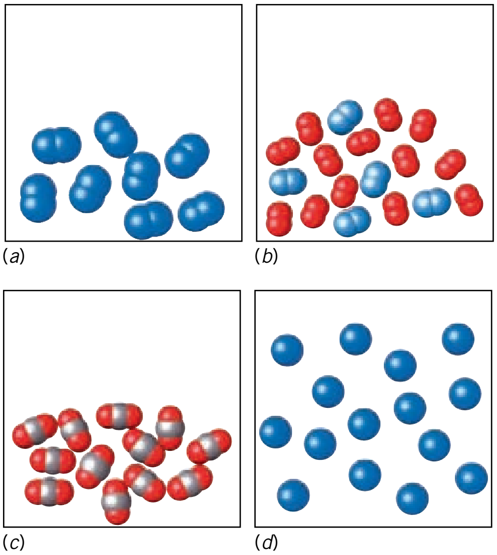
1.11 What is the chemical symbol for each of the following elements? (a) chlorine, (b) sulfur, (c) iron, (d) silver, (e) sodium, (f) phosphorus, (g) iodine, (h) copper, (i) mercury, (j) calcium

1.12 What is the name of each of the following elements? (a) K, (b) Zn, (c) Si, (d) Sn, (e) Mn, (f) Mg, (g) Ni, (h) Al, (i) C, (j) N

1.13 For each of the following molecular pictures, state whether it represents a pure substance or a mixture. For pure substances, state whether it represents an element or a compound. For mixtures, state whether it is homogeneous or heterogeneous.



1.14 Consider the following four samples of matter.



(a) Which sample(s) consist only of one element?

(b) Which sample(s) consist only of a compound?

(c) Which sample(s) consist of diatomic molecules?

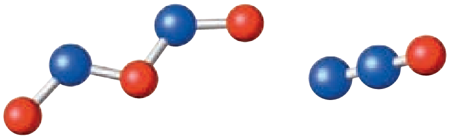
Laws of Chemical Combination and Dalton's Theory

1.15 Name and state the two laws of chemical combination discussed in this chapter.

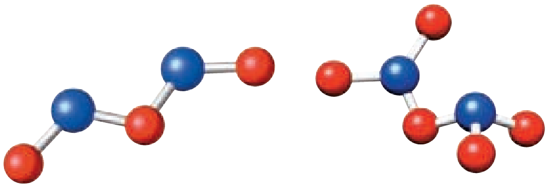
1.16 In your own words, describe how Dalton's atomic theory explains the law of conservation of mass and the law of definite proportions.

1.17 Which of the laws of chemical combination is used to define the term *compound*?

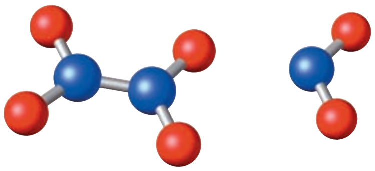
1.18 Describe the law of multiple proportions. Use the molecules illustrated below to demonstrate the law.



1.19 Explain how the following molecules demonstrate the law of multiple proportions.



1.20 Do samples containing the following molecules demonstrate the law of multiple proportions? Explain.



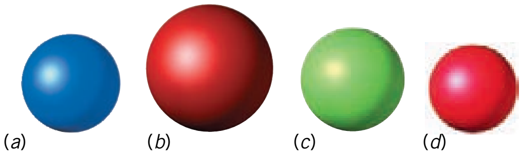
Chemical Formulas

1.21 What are two ways to interpret a chemical symbol?

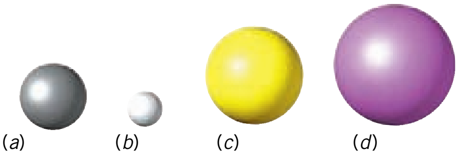
1.22 What is the difference between an atom and a molecule?

1.23 Write the formulas and names of the elements that exist in nature as diatomic molecules.

1.24 Atoms of which elements are usually represented by the following drawings? Give their names and chemical symbols.



1.25 Atoms of which elements are usually represented by the following drawings? Give their names and chemical symbols.



1.26 A DNA molecule is small in actual size but contains an enormous number of atoms. Surprisingly, the molecule is made up of atoms of just five different elements. Study Figure 1.19 and identify which elements those are.

Chemical Equations

1.27 What do we mean when we say a chemical equation is *balanced*? Why do we balance chemical equations?

1.28 For a chemical reaction, what do we mean by the term *reactants*? What do we mean by the term *products*?

1.29 The combustion of a thin wire of magnesium metal (Mg) in an atmosphere of pure oxygen produces the brilliant light of a flashbulb, once commonly used in photography. After the reaction, a thin film of magnesium oxide is seen on the inside of the bulb. The equation for the reaction is

$$2Mg + O_2 \longrightarrow 2MgO$$

(a) State in words how this equation is read.

(b) Give the formula(s) of the reactants.

(c) Give the formula(s) of the products.

Review Problems

Chemical Formulas

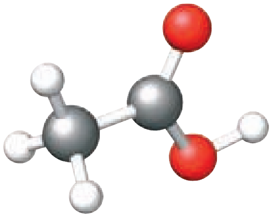
1.30 The compound $Cr(C_2H_3O_2)_3$ is used in the tanning of leather. How many atoms of each element are given in this formula?

1.31 Asbestos, a known cancer-causing agent, has a typical formula of $Ca_3Mg_5(Si_4O_{11})_2(OH)_2$. How many atoms of each element are given in this formula?

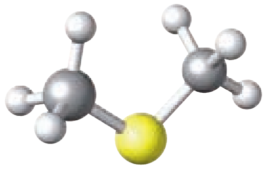
1.32 Epsom salts is a hydrate of magnesium sulfate, $MgSO_4{\cdot}7H_2O$. What is the formula of the substance that remains when Epsom salts is completely dehydrated?

1.33 Rochelle salt is the tetrahydrate of $KNaC_4H_4O_6$, which means there are four molecules of water per $KNaC_4H_4O_6$. Write the formula for Rochelle salt.

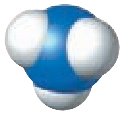
1.34 A molecule of acetic acid, formed when wine spoils and becomes sour, is shown below. Write the chemical formula for the molecule.



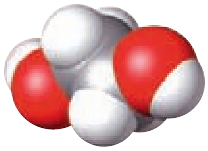
1.35 A molecule of dimethyl sulfide is shown below. The compound is a sulfurous gas with a disagreeable odor produced from breakdown products of phytoplankton through biological interactions. Write the chemical formula for the molecule. Is there a way you can write this formula using parentheses?



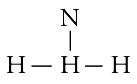
1.36 Write the chemical formula for the molecule illustrated below.



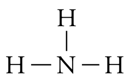
1.37 Write the chemical formula for the molecule illustrated below.



1.38 For the molecule in Problem 1.36, which of the following structural formulas is correct?

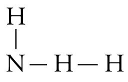
(a) 

$H-\overset{\substack{N\\|}}{H}-H$

(b) 

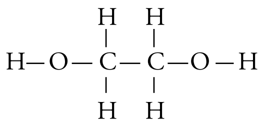
$H-\overset{\substack{H\\|}}{N}-H$

(c) $H-H-H-N$

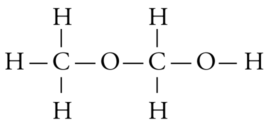
(d) 

$\overset{\substack{H\\|}}{N}-H-H$

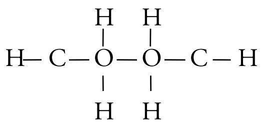
1.39 For the molecule in Problem 1.37, which of the following structural formulas is correct?

(a) 

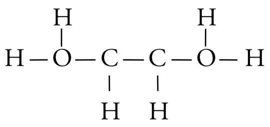
$H-O-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-O-H$

(b) 

$H-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-O-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-O-H$

(c) 

$H-C-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{O}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{O}}-C-H$

(d) 

$H-\overset{\substack{H\\|}}{O}-\underset{\substack{|\\H}}{C}-\underset{\substack{|\\H}}{C}-\overset{\substack{H\\|}}{O}-H$

1.40 How many atoms of each element are represented in each of the following formulas? For each, name the elements present. (a) $K_2C_2O_4$, (b) H_2SO_3, (c) $C_{12}H_{26}$, (d) $HC_2H_3O_2$, (e) $(NH_4)_2HPO_4$

1.41 How many atoms of each kind are represented in the following formulas? For each, name the elements present. (a) H_3PO_4, (b) $Ca(H_2PO_4)_2$, (c) C_4H_9Br, (d) $Fe_3(AsO_4)_2$, (e) $C_3H_5(OH)_3$

1.42 How many atoms of each kind are represented in the following formulas? For each, name the elements present. (a) $Ni(ClO_4)_2$, (b) $COCl_2$, (c) $K_2Cr_2O_7$, (d) CH_3CO_2H, (e) $(NH_4)_2HPO_4$

1.43 How many atoms of each kind are represented in the following formulas? For each, name the elements present. (a) $CH_3CH_2CO_2C_3H_7$, (b) $MgSO_4{\cdot}7H_2O$, (c) $KAl(SO_4)_2{\cdot}12H_2O$, (d) $Cu(NO_3)_2$, (e) $(CH_3)_3COH$

1.44 How many atoms of each element are represented in each of the following expressions?

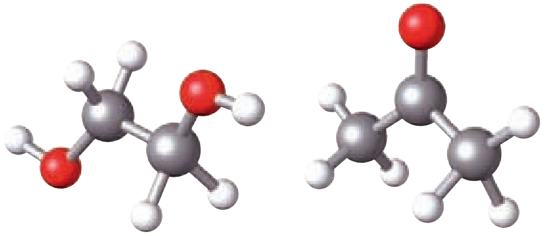
(a) $3N_2O$, (b) $4(CH_3)_2S$, (c) $2CuSO_4{\cdot}5H_2O$

OH **1.45** How many atoms of each element are represented in each of the following expressions?

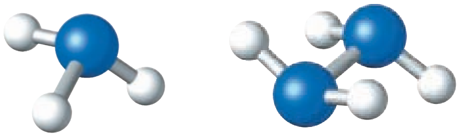
(a) $7CH_3CO_2H$, (b) $2(NH_2)_2CO$, (c) $5C_3H_5(OH)_3$

Law of Multiple Proportions

1.46 Write chemical formulas for the following molecules and explain how samples containing them can be chosen to demonstrate the law of multiple proportions.



1.47 Write chemical formulas for the following molecules and explain how samples containing them can be chosen to demonstrate the law of multiple proportions.



Chemical Equations

1.48 Consider the balanced equation

$$2Fe(NO_3)_3 + 3Na_2CO_3 \longrightarrow Fe_2(CO_3)_3 + 6NaNO_3$$

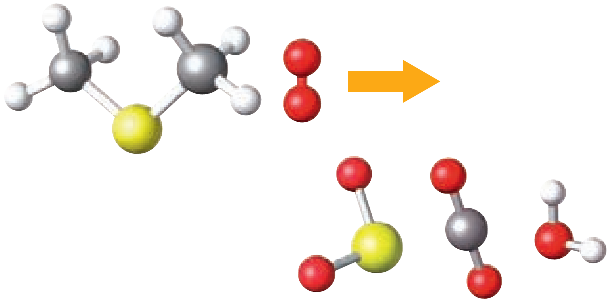
(a) How many atoms of Na are on each side of the equation?
(b) How many atoms of C are on each side of the equation?
(c) How many atoms of O are on each side of the equation?
(d) How many atoms of Fe are on each side of the equation?

1.49 Consider the balanced equation for the combustion of hexane, a component of gasoline:

$$2C_6H_{14} + 19O_2 \longrightarrow 12CO_2 + 14H_2O$$

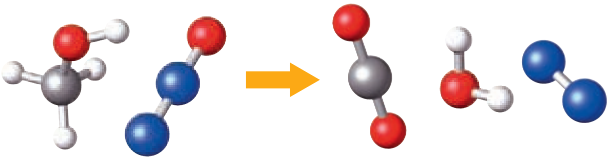
(a) How many atoms of C are on each side of the equation?
(b) How many atoms of H are on each side of the equation?
(c) How many atoms of O are on each side of the equation?

1.50 When sulfur impurities in fuels burn, they produce pollutants such as sulfur dioxide, a major contributor to acid rain. The following is a typical reaction.



On the left are reactant molecules and on the right are product molecules in a chemical reaction. How many molecules of each kind are necessary to have a balanced equation containing the smallest total number of molecules? Write the balanced chemical equation using chemical formulas.

1.51 Race car drivers can get extra power by burning methyl alcohol with nitrous oxide. Below on the left are the reactant molecules and on the right are product molecules of the chemical reaction. How many molecules of each kind are necessary to have a balanced equation containing the smallest total number of molecules? Write the balanced chemical equation using chemical formulas.

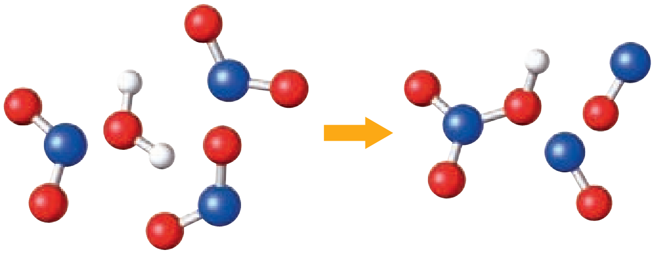


1.52 Is the following chemical equation for the combustion of octane (C_8H_{18}), a component of gasoline, balanced?

$$C_8H_{18} + 12O_2 \longrightarrow 8CO_2 + 9H_2O$$

If not, what is the smallest set of coefficients that would make the equation balanced?

1.53 Is the following chemical equation balanced? This reaction is used for the production of nitric acid, HNO_3, and is one of the reactions responsible for acid rain.



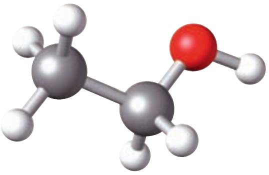
$$3NO_2 + H_2O \longrightarrow HNO_3 + 2NO$$

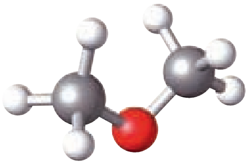
If the equation is not balanced, find coefficients that would make it balanced.

Additional Exercises

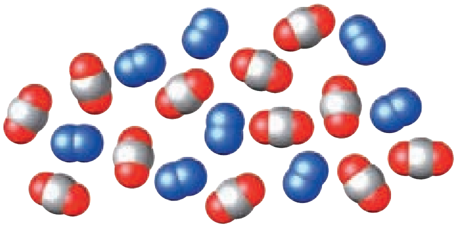
1.54 How would you explain that the following molecules follow the law of multiple proportions? N_2O, NO_2

1.55 The following are models of molecules of two compounds composed of carbon, hydrogen, and oxygen. The one on the left is ethanol, the alcohol that's added to gasoline with the hope of reducing our dependence on foreign oil supplies. The one on the right is dimethyl ether, a compound that is a gas at room temperature and is used as an aerosol propellant. How many atoms of carbon, hydrogen, and oxygen are in each of these molecules? Find a way to write the formula of one of them using parentheses so that the two compounds can be distinguished one from the other.


ethyl alcohol


dimethyl ether

1.56 A student obtained a sample from an experiment that had the folowing composition:



If the experiment were repeated and another sample were obtained, would it have to have the exact same composition? Would the results of these experiments illustrate the law of definite proportions? Explain.

1.57 Suppose you wanted to separate the sample illustrated in the preceding question into its constituent chemical elements. (a) Would a physical change be sufficient? (b) If not, what could be accomplished by a physical change? (c) Would a chemical change be required? (d) If so, on which substance would a chemical change have to be applied? (e) Would the elements isolated by these changes necessarily be composed of individual atoms, or would at least one be composed of molecules?

Exercises in Critical Thinking

1.58 A solution is defined as a uniform mixture consisting of a single phase. With our vastly improved abilities to "see" smaller and smaller particles, down to the atomic level, present an argument for the proposition that all mixtures are heterogeneous. Present the argument that the ability to observe objects as small as an atom has no effect on the definitions of heterogeneous and homogeneous.

1.59 How do you know that Coca Cola is not a compound? What experiments could you perform to prove it? What would you do to prove that the rusting of iron is a chemical change rather than a physical change?

2 Scientific Measurements

Chapter Outline

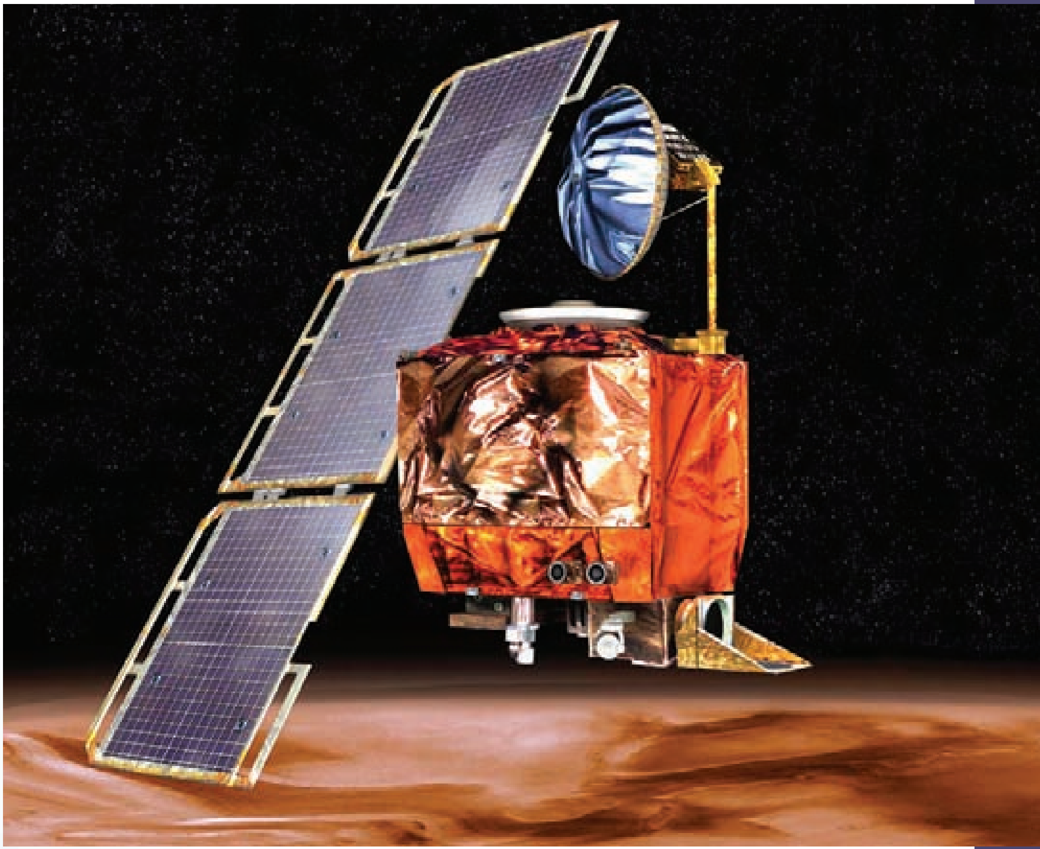
2.1 | Physical and Chemical Properties

2.2 | Measurement of Physical and Chemical Properties

2.3 | The Uncertainty of Measurements

2.4 | Dimensional Analysis

2.5 | Density and Specific Gravity



The grand photos and artist's renderings of spacecraft reaching the moon, planets, and outer reaches of the solar system are familiar to all. The achievement is remarkable because it has been a little over one hundred years since powered flight was achieved. Along with the grandeur come the details. On September 23, 1999, the Mars Climate Orbiter crashed into the surface of Mars. On September 30, NASA announced that the cause of the accident was a mix-up in measurement units. Although computers can transfer numbers easily, units are more difficult. Without the units, scientists were unaware that their calculations were in error, and the spacecraft was given incorrect instructions. This incident simply highlights the central theme of this chapter, which emphasizes the use of units along with numbers in all calculations. (NASA/JPL)

This Chapter in Context

In Chapter 1 we saw that chemistry is an atomic and molecular science. One of the basic tenets of chemistry is that if we understand the nature of our atoms and molecules on the microscopic scale, we will be able to understand the properties of chemicals on the macroscopic scale. We obtain this understanding by making precise observations and numerical measurements.

At this point in time, scientists have become very systematic in making and reporting measurements. As we will see in this chapter, we need to understand which physical and chemical properties are important to measure. Then we will find that of all the many measurements we can make, there are only seven basic units, in various combinations, that describe all of them. Finally, we will see that once we make our measurements there are certain rules to follow so that the answers to our calculations will be reported correctly.

This chapter has three principal goals. The first is to provide you with an appreciation of the nature of and distinction between physical and chemical properties. The second is to explain the way scientists approach the process of making quantitative experimental observations of these properties. The third goal is to describe the accepted methods for treating experimental data.

2.1 | Physical and Chemical Properties

■ As in Chapter 1, some material may be familiar from a past science course. This chapter emphasizes that mathematics is an important tool for success in chemistry. A very good working knowledge of algebra will be important as we progress.

In chemistry we use **properties** (characteristics) of materials to identify them and to distinguish one substance from another. To help organize our thinking, we classify properties into two different types, physical and chemical.

Physical Properties

One way to classify properties is based on whether or not the chemical composition of an object is changed by the act of observing the property. *A* **physical property** *is one that can be observed without changing the chemical makeup of a substance.* For example, a physical property of gold is that it is yellow. The act of observing this property (color) doesn't change the chemical makeup of the gold. Neither does observing that gold conducts electricity, so color and electrical conductivity are physical properties.

Sometimes, observing a physical property does lead to a physical change. To measure the melting point of ice, for example, we observe the temperature at which the solid begins to melt (Figure 2.1). This is a physical change because it does not lead to a change in chemical composition; both ice and liquid water are composed of water molecules.

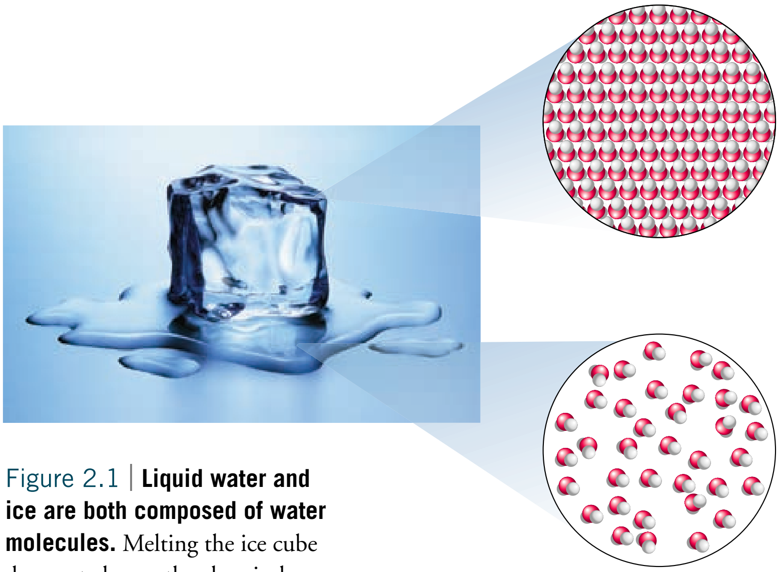


Figure 2.1 | **Liquid water and ice are both composed of water molecules.** Melting the ice cube does not change the chemical composition of the molecules. *(Daniel Smith/Corbis)*

States of Matter

When we observe ice melting, we see two states of matter, liquid and solid. Water can also exist as a gas that we call water vapor or steam. Although ice, liquid water, and steam have quite different appearances and physical properties, they are just different forms of the same substance, water. **Solid, liquid,** and **gas** are the most common **states of matter.** As with water, most substances are able to exist in all three of these states, and the state we observe generally depends on the temperature. The obvious properties of solids, liquids, and gases can be interpreted at a submicroscopic level according to the different ways the individual atomic-size particles are organized (Figure 2.2). For a given substance, a change from one state to another is a physical change.

In Chapter 1 we discussed chemical equations. We saw that they must obey the law of conservation of mass by being balanced. We also saw that these equations represented the actual interaction of atoms and molecules. An additional refinement of the chemical equation that we can make is to specify the state of each substance. For instance, we can rewrite the combustion reaction for butane and include the states of each substance.

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

Each of the substances is followed by (g) to show it is in the gas state, since butane burns at a temperature above the boiling point of water. In a similar way we can indicate that a substance is a solid with (s) or a liquid with (l).

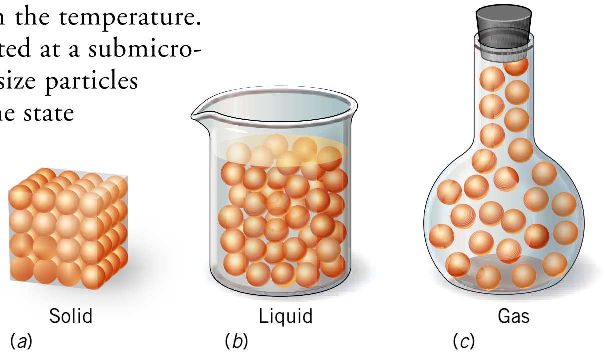


Figure 2.2 | **Solid, liquid, and gaseous states viewed using the atomic model of matter.** (*a*) In a solid, the particles are tightly packed and cannot move easily. (*b*) In a liquid, the particles are still close together but can readily move past one another. (*c*) In a gas, particles are far apart with much empty space between them.

Chemical Properties

A **chemical property** *describes a chemical change (chemical reaction) that a substance undergoes.* When a chemical reaction takes place, chemicals interact to form entirely *different* substances with different chemical and physical properties. An example is the rusting of iron, which involves a chemical reaction between iron, oxygen, and water. When these three react, the product, rust, no longer looks like iron, oxygen, or water. It's a brown solid that isn't at all like a metal, and it is not attracted by a magnet (Figure 2.3).

The ability of iron to form rust in the presence of oxygen and moisture is a chemical property of iron. When we observe this property, the reaction changes the iron, oxygen, and water into rust, so after we've made the observation we no longer have the same substances as before. In describing a chemical property, we usually refer to a chemical reaction.

In modern science, we often want to know whether a substance presents a health hazard before we use it. Health hazards of materials are usually a type of chemical property whereby a substance will have an adverse effect on one or more of the many chemical reactions within our bodies. Toxicology is a field of science that depends heavily on chemical principles to assess the effects of poisons and toxins on living organisms.

Figure 2.3 | **Chemical reactions cause changes in composition.** Here we see a coating of rust that has formed on an iron object. The properties and chemical composition of the rust are entirely different from those of the iron. *(George B. Diebold/Corbis Images)*

Intensive and Extensive Properties

Another way of classifying a property is according to whether or not it depends on the size of the sample. For example, two different pieces of gold can have different volumes, but both have the same characteristic shiny yellow color and both will begin to melt at the same temperature. Color and melting point (and boiling point, too) are examples of **intensive properties**—*properties that are independent of sample size.* Volume, on the other hand, is an **extensive property**—*a property that depends on sample size.* Mass is another extensive property.

A job chemists often perform is *chemical analysis*. They're asked, "What is a particular sample composed of?" To answer such a question, the chemist relies on the properties of the chemicals that make up the sample. For identification purposes, intensive properties are more useful than extensive ones because every sample of a given substance exhibits the same set of intensive properties.

Color, freezing point, and boiling point are examples of intensive physical properties that can help us identify substances. Chemical properties are also intensive properties and also can be used for identification. For example, gold miners were able to distinguish between real gold and fool's gold, a mineral also called pyrite (Figure 1.8, page 8), by heating the material in a flame. Nothing happens to the gold, but the pyrite sputters, smokes, and releases bad-smelling fumes because of its ability, when heated, to react chemically with oxygen in the air.

2.2 | Measurement of Physical and Chemical Properties

Qualitative and Quantitative Observations

Earlier you learned that an important step in the scientific method is observation. In general, observations fall into two categories, qualitative and quantitative. **Qualitative observations**, such as the color of a chemical or that a mixture becomes hot when a reaction occurs, do not involve numerical information. **Quantitative observations** are those **measurements** that do yield numerical data. You make such observations in everyday life, for example, when you glance at your watch or step onto a bathroom scale. In chemistry, we make various measurements that aid us in describing both chemical and physical properties.

Measurements Include Units

Measurements involve numbers, but they differ from the numbers used in mathematics in two crucial ways.

First, measurements always involve a comparison. When you say that a person is six feet tall, you're really saying that the person is six times taller than a reference object that is 1 foot high, where *foot* is an example of a **unit of measurement**. *Both the number and the unit are essential parts of the measurement,* because the unit gives the reported value a sense of size. For example, if you were told that the distance between two points is 25, you would naturally ask "25 what?" The distance could be 25 inches, 25 feet, 25 miles, or 25 of any other unit that's used to express distance. A number without a unit is really meaningless. *Writing down a measurement without a unit is a common and serious mistake, and one you should avoid.*

The second important difference is that measurements always involve uncertainty; they are *inexact*. The act of measurement involves an estimation of one sort or another, and both the observer and the instruments used to make the measurement have inherent physical limitations. As a result, measurements always include some uncertainty, which can be minimized but never entirely eliminated. We will say more about this topic in Section 2.3.

International System of Units (SI Units)

A standard system of units is essential if measurements are to be made consistently. In the sciences, and in virtually every nation on Earth, except the United States, metric-based units are used. The advantage of working with metric units is that converting to larger or smaller values can be done simply by moving a decimal point, because metric units are related to each other by simple multiples of ten.

In 1960, a simplification of the original metric system was adopted by the General Conference on Weights and Measures (an international body). It is called the **International System of Units**, abbreviated **SI** from the French name, *Le Système International d'Unités*. The SI is now the dominant system of units in science and engineering, although there is still some usage of older metric units.

The SI has as its foundation a set of **base units** (Table 2.1) for seven measured quantities. For now, we will focus on the base units for length, mass, time, and temperature. We will discuss the unit for amount of substance, the mole, at length in Chapter 4. The unit for electrical current, the ampere, will be discussed briefly when we study electrochemistry in Chapter 20. The unit for luminous intensity, the candela, will not be discussed in this book.

Most of the base units are defined in terms of reproducible physical phenomena. For instance, the meter is defined as exactly the distance light travels in a vacuum in 1/299,792,458 of a second. Everyone has access to this standard because light and a vacuum

Table 2.1 The SI Base Units

Measurement	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

TOOLS Base SI units

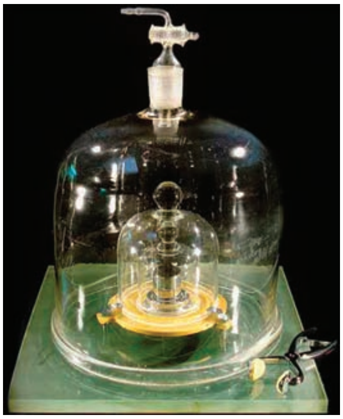


Figure 2.4 | **The international standard kilogram.** The SI standard for mass is made of a platinum–iridium alloy and is protected under two bell jars, as shown, at the International Bureau of Weights and Measures in France. Precise copies, called secondary standards, are maintained by many countries. *(NIST)*

are available to all. Only the base unit for mass is defined by an object made by human hands. It is a carefully preserved platinum–iridium alloy block stored at the International Bureau of Weights and Measures in France (Figure 2.4). This block serves indirectly as the calibrating standard for all "weights" used for scales and balances throughout the world.[1]

In scientific measurements, *all* physical quantities will have units that are combinations of the seven base SI units. For example, there is no SI base unit for area, but we know that to calculate the area of a rectangular room we multiply its length by its width. Therefore, the *unit* for area is derived by multiplying the *unit* for length by the *unit* for width. Length and width are each a measurement that have the SI base unit of the **meter (m)**.

$$\text{length} \times \text{width} = \text{area}$$
$$(\text{meter}) \times (\text{meter}) = (\text{meter})^2$$
$$\text{m} \times \text{m} = \text{m}^2$$

The SI **derived unit** for area is therefore m^2 (read as *meters squared*, or *square meter*).

In deriving SI units, we employ a very important concept that we will use repeatedly throughout this book when we perform calculations: *Units undergo the same kinds of mathematical operations that numbers do.* We will see how this fact can be used to convert from one unit to another in Section 2.4.

Example 2.1
Deriving SI Units

Linear momentum is a measure of the "push" a moving object has, equal to the object's mass times its velocity. What is the SI derived unit for linear momentum?

■ **Analysis:** To derive a unit for a quantity we must first express it in terms of simpler quantities. We're told that linear momentum is mass times velocity. Therefore, the SI unit for linear momentum will be the SI unit for mass times the SI unit for velocity. Since velocity is not one of the base SI units, we will need to find the SI units for velocity.

■ **Assembling the Tools:** The only tool we need for this question is the list of SI base units in Table 2.1. We will also have to recall that velocity is distance traveled (length) per unit time. The tools are:

SI unit for mass is the kg

SI units for velocity (length/time) are m/s

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[1] Scientists are working on a method of accurately counting atoms whose masses are accurately known. Their goal is to develop a new definition of the kilogram that doesn't depend on an object that can be stolen, lost, or destroyed.

Solution: We start by expressing the given information as an equation:

$$\text{mass} \times \text{velocity} = \text{linear momentum}$$

Next we write the same equation with units because units undergo the same mathematical operations as the numbers.

$$\text{kg} \times \text{m/s} = \text{kg m/s} \qquad \text{or} \qquad \text{kg m s}^{-1}$$

Our result is that linear momentum has units of kg m/s or kg m s^{-1}.

Is the Answer Reasonable? *Before leaving a problem, it is always wise to examine the answer to see whether it makes sense.* For numerical calculations, ask yourself, "Is the answer too large or too small?" Judging the answers to such questions serves as a check on the arithmetic as well as on the method of obtaining the answer. It can help you find obvious errors. In this problem, the check is simple. The derived unit for linear momentum should be the product of units for mass and velocity, and this is obviously true. Therefore, our answer is correct.

Practice Exercises

2.1 | The volume of a sphere is given by the formula $V = \frac{4}{3}\pi r^3$, where r is the radius of the sphere. From this equation, determine the SI units for volume. (*Hint: r* is a length, so it must have a length unit.)

2.2 | When you "step hard on the gas" in a car you feel an invisible force pushing you back in your seat. This force, F, equals the product of your mass, m, times the acceleration, a, of the car. In equation form, this is $F = ma$. Acceleration is the change in velocity, v, with time, t:

$$a = \frac{\text{change in } v}{\text{change in } t}$$

Therefore, the units of acceleration are those of velocity divided by time. What is the SI derived unit for force expressed SI base units?

Non-SI Units

Some older metric units that are not part of the SI system are still used in the laboratory and in the scientific literature. Some of these units are listed in Table 2.2; others will be introduced as needed in upcoming chapters.

Many of the "English" measurements are now defined based on the SI base units.

The United States is the only large nation still using the **English system** of units, which measures distance in inches, feet, and miles; volume in ounces, quarts, and gallons; and mass in ounces and pounds. However, a gradual transition to metric units is occurring and, in fact, many of the English units are defined with reference to base SI units. Beverages,

Table 2.2 Some Non-SI Metric Units Commonly Used in Chemistry

Measurement	Name	Symbol	Value in SI Units
Length	angstrom	Å	1 Å = 0.1 nm = 10^{-10} m
Mass	atomic mass unit	u (amu)	1 u = 1.66054×10^{-27} kg, approximately
	metric ton	t	1 t = 10^3 kg
Time	minute	min.	1 min. = 60 s
	hour	h (hr)	1 h = 60 min. = 3600 s
Temperature	degree Celsius	°C	$T_K = t_{°C} + 273.15$
Volume	liter	L	1 L = 1000 cm^3

Table 2.3 Some Useful Conversions

Measurement	English Unit	English/SI Equality[a]
Length	inch	1 in. = 2.54 cm
	yard	1 yd = 0.9144 m
	mile	1 mi = 1.609 km
Mass	pound	1 lb = 453.6 g
	ounce (mass)	1 oz = 28.35 g
Volume	gallon	1 gal = 3.785 L
	quart	1 qt = 946.4 mL
	ounce (fluid)	1 oz = 29.6 mL

[a] These equalities allow us to convert English to metric or metric to English units.

food packages, tools, and machine parts are often labeled in metric units (Figure 2.5). Common conversions between the English system and the SI are given in Table 2.3 and inside the back cover of this book.[2]

355mL
454g
454g
1 liter

Figure 2.5 | **Metric units are becoming commonplace on most consumer products.** *(Michael Watson)*

Decimal Multipliers

Sometimes the basic units are either too large or too small to be used conveniently. For example, the meter is inconvenient for expressing the size of very small things such as bacteria. The SI solves this problem by forming larger or smaller units by applying **decimal multipliers** to the base units. Table 2.4 lists the most commonly used decimal multipliers and the prefixes used to identify them.

Table 2.4 SI Prefixes—Their meanings and values[a]

Prefix	Meaning	Symbol	Prefix Value[b] (numerical)	Prefix Value[b] (power of ten)
exa		E		10^{18}
peta		P		10^{15}
tera		T		10^{12}
giga	**billions of**	**G**	**1000000000**	$\mathbf{10^{9}}$
mega	**millions of**	**M**	**1000000**	$\mathbf{10^{6}}$
kilo	**thousands of**	**k**	**1000**	$\mathbf{10^{3}}$
hecto		h		10^{2}
deka		da		10^{1}
deci	**tenths of**	**d**	**0.1**	$\mathbf{10^{-1}}$
centi	**hundredths of**	**c**	**0.01**	$\mathbf{10^{-2}}$
milli	**thousandths of**	**m**	**0.001**	$\mathbf{10^{-3}}$
micro	**millionths of**	μ	**0.000001**	$\mathbf{10^{-6}}$
nano	**billionths of**	**n**	**0.000000001**	$\mathbf{10^{-9}}$
pico	**trillionths of**	**p**	**0.000000000001**	$\mathbf{10^{-12}}$
femto		f		10^{-15}
atto		a		10^{-18}

[a] Prefixes in bold type are used most often.

[b] Numbers in these columns can be interchanged with the corresponding prefix.

TOOLS

SI prefixes

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[2] Originally, these conversions were established by measurement. For example, if a metric ruler is used to measure the length of an inch, it is found that 1 in. equals 2.54 cm. Later, to avoid confusion about the accuracy of such measurements, it was agreed that these relationships would be taken to be exact. For instance, 1 in. is now defined as *exactly* 2.54 cm. Exact relationships also exist for the other quantities, but for simplicity many have been rounded off. For example, 1 lb = 453.59237 g, *exactly*.

■ A modified base unit can be conveniently converted to the base unit by removing the prefix and inserting × 10^x.

$$25.2 \text{ pm} = 25.2 \times 10^{-12} \text{ m}$$

A prefix can be inserted by adjusting the exponential part of a number to match the definition of a prefix. Then the exponent is removed and replaced by the prefix.

$$2.34 \times 10^{10} \text{ g} = 23.4 \times 10^{9} \text{ g} = 23.4 \text{ Gg}$$

When the name of a unit is preceded by one of these prefixes, the size of the unit is modified by the corresponding decimal multiplier. For instance, the prefix *kilo* indicates a multiplying factor of 10^3, or 1000. Therefore, a *kilo*meter is a unit of length equal to 1000 meters.[3] The symbol for kilometer (km) is formed by applying the symbol meaning kilo (k) as a prefix to the symbol for meter (m). Thus 1 km = 1000 m (or alternatively, 1 km = 10^3 m). Similarly a decimeter (dm) is 1/10th of a meter, so 1 dm = 0.1 m (1 dm = 10^{-1} m).

The symbols and multipliers are listed in Table 2.4. Those listed in boldface type are the ones most commonly encountered in chemistry.

Laboratory Measurements

TOOLS

Units for laboratory measurements

The most common measurements you will make in the laboratory will be those of length, volume, mass, and temperature.

Length

The SI base unit for length, the **meter (m)**, is too large for most laboratory purposes. More convenient units are the **centimeter (cm)** and the **millimeter (mm)**. Using Table 2.4 we see that they are related to the meter as follows.

$$1 \text{ cm} = 10^{-2} \text{ m} = 0.01 \text{ m}$$
$$1 \text{ mm} = 10^{-3} \text{ m} = 0.001 \text{ m}$$

It is also useful to know the relationships

$$1 \text{ m} = 100 \text{ cm} = 1000 \text{ mm}$$
$$1 \text{ cm} = 10 \text{ mm}$$

■ An older, non-SI unit called the angstrom (Å) is often used to describe dimensions of atomic- and molecular-sized particles.

$$1 \text{ Å} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

Volume

Volume is a derived unit with dimensions of $(\text{length})^3$. With these dimensions expressed in meters, the derived SI unit for volume is the **cubic meter, m^3**.

In chemistry, measurements of volume usually arise when we measure amounts of liquids. The traditional metric unit of volume used for this is the **liter (L)**. In SI terms, a liter is defined as exactly 1 cubic decimeter.

$$1 \text{ L} = 1 \text{ dm}^3 \text{ (exactly)} \qquad \textbf{(2.1)}$$

However, even the liter is too large to conveniently express most volumes measured in the lab. The glassware we normally use, as illustrated in Figure 2.6, is marked in **milliliters (mL).**[4]

$$1 \text{ L} = 1000 \text{ mL}$$

Because 1 dm = 10 cm, then 1 dm^3 = 1000 cm^3. Therefore, 1 mL is exactly the same as 1 cm^3.

$$1 \text{ cm}^3 = 1 \text{ mL}$$
$$1 \text{ L} = 1000 \text{ cm}^3 = 1000 \text{ mL}$$

Sometimes you may see cm^3 abbreviated cc (especially in medical applications), although the SI frowns on this symbol. Figure 2.7 compares the cubic meter, liter, and milliliter.

---

[3] In the sciences, powers of 10 are often used to express large and small numbers. The quantity 10^3 means $10 \times 10 \times 10 = 1000$. Similarly, the quantity $6.5 \times 10^2 = 6.5 \times 100 = 650$. Numbers less than 1 have negative exponents when expressed as powers of 10. Thus, the fraction $\frac{1}{10}$ is expressed as 10^{-1}, so the quantity 10^{-3} means $\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} = \frac{1}{1000}$. A value of $6.5 \times 10^{-3} = 6.5 \times 0.001 = 0.0065$. Numbers written as 6.5×10^2 and 6.5×10^{-3}, with the decimal point between the first and second digit, are said to be expressed in **scientific notation**.

[4] Use of the abbreviations L for liter and mL for milliliter is rather recent. Confusion between the printed letter l and the number 1 prompted the change from l to L and ml to mL. You may encounter the abbreviation ml in other books or on older laboratory glassware.

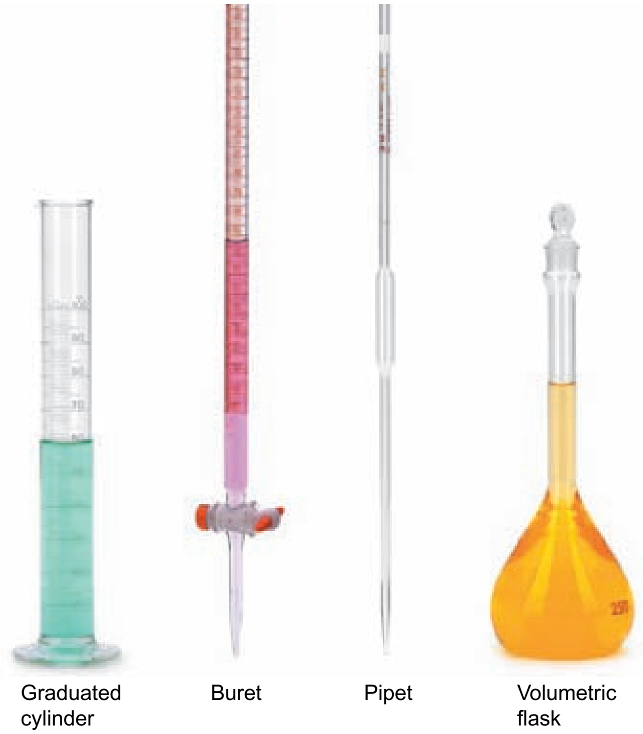


Figure 2.6 | **Common laboratory glassware used for measuring volumes.** Graduated cylinders are used for measuring volumes to the nearest milliliter. Precise measurements of volumes are made using burets, pipets, and volumetric flasks. *(Andy Washnik)*

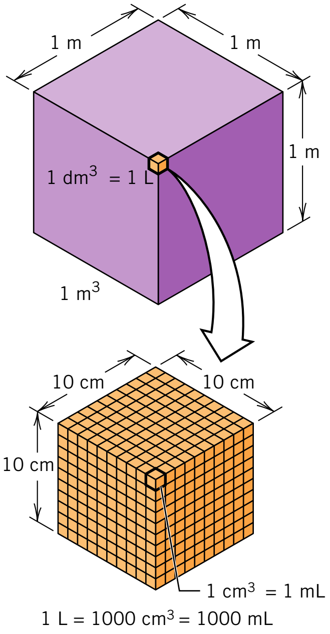


Figure 2.7 | **Comparing volume units.** A cubic meter (m^3) is approximately equal to a cubic yard. 1000 cm^3 is approximately a quart, and approximately 30 cm^3 is equal to one fluid ounce.

Mass

In the SI, the base unit for mass is the **kilogram (kg)**, although the **gram (g)** is a more conveniently sized unit for most laboratory measurements. One gram, of course, is $\frac{1}{1000}$ of a kilogram (1 kilogram = 1000 g, so 1 g must equal 0.001 kg).

Mass is measured by comparing the weight of a sample with the weights of known standard masses. (Recall from Chapter 1 that mass and weight are not the same thing.) The instrument used is called a **balance** (Figure 2.8). For the balance in Figure 2.8*a*, we

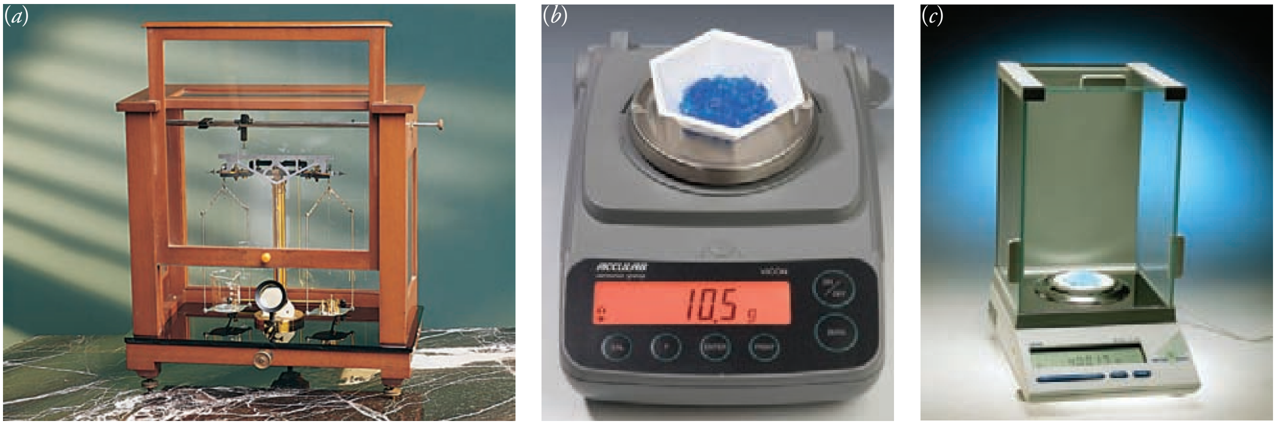


Figure 2.8 | **Typical laboratory balances.** (*a*) A traditional two-pan analytical balance capable of measurements to the nearest 0.0001 g. (*b*) A modern top-loading balance capable of mass measurements to the nearest 0.1 g. (*c*) A modern analytical balance capable of measurements to the nearest 0.0001 g. *(Michael Watson; © 2005 Richard Megna/Fundamental Photographs; Charles D. Winters/Photo Researchers)*

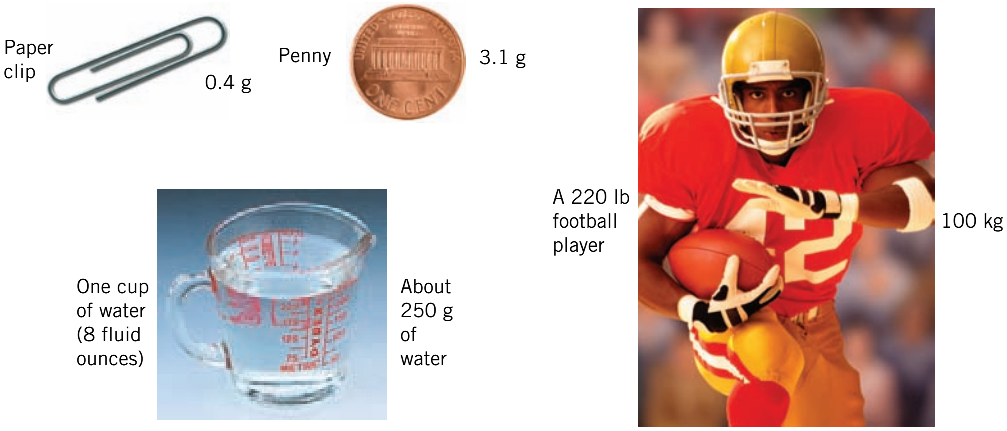


Figure 2.9 | **Masses of several common objects.** *(iStockphoto; iStockphoto; Andy Washnik; Jim Cummins/Taxi/Getty Images, Inc.)*

would place our sample on the left pan and then add standard masses to the other. When the weight of the sample and the total weight of the standards are in balance (when they match), their masses are then equal. Figure 2.9 shows the masses of some common objects in SI units.

Temperature

■ In chemistry, reference data are commonly tabulated at 25 °C, which is close to room temperature. Biologists often carry out their experiments at 37 °C because that is our normal body temperature.

Temperature is usually measured with a thermometer (Figure 2.10). Thermometers are graduated in *degrees* according to one of two temperature scales. On the **Fahrenheit scale** water freezes at 32 °F and boils at 212 °F. If you've been raised in the United States, this is probably the scale you're most familiar with. In recent times, however, you have probably noticed an increased use of the **Celsius scale**, especially in weather broadcasts. This is the scale we use most often in the sciences. On the Celsius scale water freezes at 0 °C and boils at 100 °C. (See Figure 2.11.)

As you can see in Figure 2.11, on the Celsius scale there are 100 degree units between the freezing and boiling points of water, while on the Fahrenheit scale this same temperature range is spanned by 180 degree units. Consequently, 5 Celsius degrees are the same as 9 Fahrenheit degrees. We can use the following equation as a tool to convert between these temperature scales.

TOOLS

Celsius to Fahrenheit conversion

$$t_F = \left(\frac{9\ °F}{5\ °C}\right)t_C + 32\ °F \tag{2.2}$$

In this equation, t_F is the Fahrenheit temperature and t_C is the Celsius temperature. As noted earlier, units behave like numbers in calculations, and we see in Equation 2.2 that

(a)
10
0
10
20
30
40
50
60
70
80
90
100
(b)
F

Figure 2.10 | **Typical laboratory thermometers.** (*a*) A traditional mercury thermometer. (*b*) An electronic thermometer. *(Michael Watson; Corbis Images)*

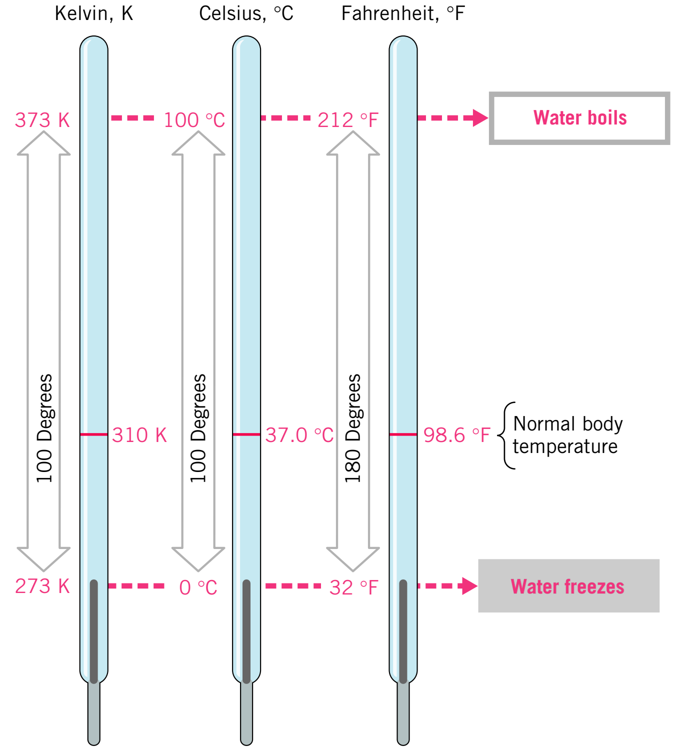


Figure 2.11 | **Comparison among Kelvin, Celsius, and Fahrenheit temperature scales.**

°C "cancels out" to leave only °F. The 32 °F is added to account for the fact that the freezing point of water (0 °C) occurs at 32 °F on the Fahrenheit scale. Equation 2.2 can easily be rearranged to permit calculating the Celsius temperature from the Fahrenheit temperature.

The SI unit of temperature is the **kelvin (K)**, which is the degree unit on the **Kelvin temperature scale**. Notice that the temperature unit is K, not °K (the degree symbol, °, is omitted). Also notice that the name of the unit, kelvin, is not capitalized. Equations that include temperature as a variable sometimes take on a simpler form when Kelvin temperatures are used. We will encounter this situation many times throughout the book.

■ The name of the temperature scale, the Kelvin scale, is capitalized, but the name of the unit, the kelvin, is not. However, the symbol for the kelvin is a capital K.

Figure 2.11 shows how the Kelvin, Celsius, and Fahrenheit temperature scales relate to each other. Notice that the kelvin is *exactly* the same size as the Celsius degree. *The only difference between these two temperature scales is the zero point.* The zero point on the Kelvin scale is called **absolute zero** and corresponds to nature's lowest temperature. It is 273.15 degree units below the zero point on the Celsius scale, which means that 0 °C equals 273.15 K, and 0 K equals −273.15 °C. Common laboratory thermometers are never marked with the Kelvin scale, so to convert from Celsius to Kelvin temperatures the following equation applies.

$$T_K = (t_C + 273.15)\,\cancel{°C}\,\frac{1\ K}{1\ \cancel{°C}} \qquad \textbf{(2.3)}$$

TOOLS

Celsius to Kelvin conversion

This amounts to simply adding 273.15 to the Celsius temperature to obtain the Kelvin temperature. Often we are given Celsius temperatures rounded to the nearest degree, in which case we round 273.15 to 273. Thus, 25 °C equals (25 + 273) K or 298 K.

■ We will use a capital T to stand for the Kelvin temperature and a lowercase t (as in t_C) to stand for the Celsius temperature. This conforms to the usage described by the International Bureau of Weights and Measures in Sevres, France, and the National Institute of Standards and Technology in Gaithersburg, Maryland.

Types of Mathematical Calculations

We will discuss many problems throughout the book that require mathematical calculations. In approaching them you will see that they can be divided into two general types. The type described in Example 2.2 involves applying a mathematical equation in which we have numerical values for all but one of the variables in the equation. To perform the calculation, we solve the equation by substituting known values for the variables until there is only one unknown variable that can be calculated. The second type of calculation that we will encounter, which is described in detail in Section 2.4, is one where we convert one set of units into another set of units using a method called dimensional analysis.

If you follow our approach of *Analysis and Assembling the Tools*, the nature of the types of calculations involved should become apparent. As you will see, some problems involve both kinds of calculations.

Example 2.2
Converting among Temperature Scales

Thermal pollution, the release of large amounts of heat into rivers and other bodies of water, is a serious problem near power plants and can affect the survival of some species of fish. For example, trout will die if the temperature of the water rises above approximately 25 °C. (a) What is this temperature in °F? (b) Rounded to the nearest whole degree unit, what is this temperature in kelvins?

■ **Analysis:** Both parts of the problem here deal with temperature conversions. Therefore, we ask ourselves, "What tools do we have that relate temperature scales to each other?" We have just seen two of these tools.

■ **Assembling the Tools:** The first tool, Equation 2.2, relates Fahrenheit temperatures to Celsius temperatures, so this is the tool we need to answer part (a).

$$t_F = \left(\frac{9\ °\mathrm{F}}{5\ °\mathrm{C}}\right) t_C + 32\ °\mathrm{F}$$

Equation 2.3 relates Kelvin temperatures to Celsius temperatures, so this is the tool we need for part (b).

$$T_K = (t_C + 273.15)\ °\mathrm{C}\left(\frac{1\ \mathrm{K}}{1\ °\mathrm{C}}\right)$$

■ **Solution:**

Part (a): We substitute the value of the Celsius temperature (25 °C) for t_C and calculate the answer

$$t_F = \left(\frac{9\ °\mathrm{F}}{5\ \cancel{°\mathrm{C}}}\right)(25\ \cancel{°\mathrm{C}}) + 32\ °\mathrm{F}$$

$$= 45\ °\mathrm{F} + 32\ °\mathrm{F} = 77\ °\mathrm{F}$$

Therefore, 25 °C = 77 °F. (Notice that we have canceled the unit °C in the equation above.)

Part (b): Once again, we have a simple substitution. Since $t_C = 25$ °C, the Kelvin temperature (rounded) is calculated as

$$T_K = (25\ °\mathrm{C} + 273\ °\mathrm{C})\left(\frac{1\ \mathrm{K}}{1\ °\mathrm{C}}\right)$$

$$= 298\ \cancel{°\mathrm{C}}\left(\frac{1\ \mathrm{K}}{1\ \cancel{°\mathrm{C}}}\right) = 298\ \mathrm{K}$$

Thus, 25 °C = 298 K.

Are the Answers Reasonable? For part (a), we know that a Fahrenheit degree is about half the size of a Celsius degree, so 25 Celsius degrees should be about 50 Fahrenheit degrees. The positive value for the Celsius temperature tells us we have a temperature *above* the freezing point of water. Since water freezes at 32 °F, the Fahrenheit temperature should be approximately 32 °F + 50 °F = 82 °F. The answer of 77 °F is quite close.

For part (b), we recall that 0 °C = 273 K. A temperature above 0 °C must be higher than 273 K. Our calculation, therefore, appears to be correct.

Practice Exercises

2.3 | What Fahrenheit temperature corresponds to a Celsius temperature of 86 °C? (*Hint:* What tool relates these two temperature scales?)

2.4 | What Celsius temperature corresponds to 50 °F? What Kelvin temperature corresponds to 68 °F (expressed to the nearest whole kelvin unit)?

2.3 | The Uncertainty of Measurements

We noted in the preceding section that measurements are inexact; they contain **uncertainties** (also called **errors**). One source of uncertainty is associated with limitations in our ability to read the scale of the measuring instrument. Uncontrollably changing conditions at the time of the measurement can also cause errors that are more important than scale-reading errors. For example, if you are measuring a length of wire with a ruler, you may not be holding the wire perfectly straight every time.

If we were to take an enormous number of measurements using appropriately adjusted instruments, statistically half of the measurements should be larger and half smaller than the true value of the measured quantity. In fact, we do observe that a repetitive series of measurements tends to give results that cluster around a central value, which we generally assume is close to the true value. We can estimate the central value quite simply by reporting the **average**, or **mean**, of the series of measurements. This is done by summing the measurements and then dividing by the number of measurements we made. Although making repeated measurements is tedious, the more measurements we make, the more confident we can be that the average is close to the true value.

Uncertainties in Measurements

One kind of error that cannot be eliminated arises when we attempt to obtain a measurement by reading the scale on an instrument. Consider, for example, reading the same temperature from each of the two thermometers in Figure 2.12.

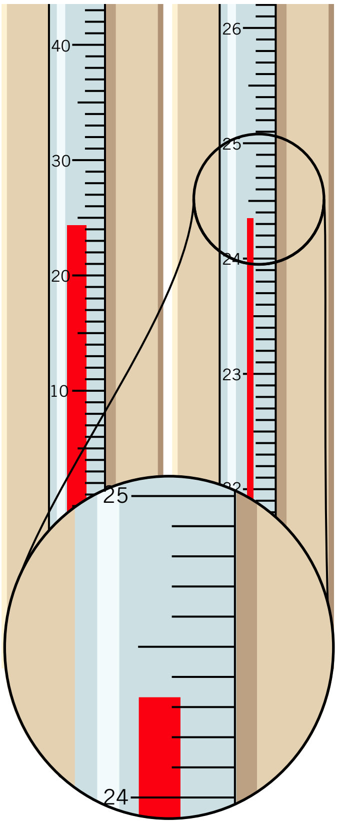


Figure 2.12 | **Thermometers with different scales give readings with different precision.** The thermometer on the left has marks that are one degree apart, allowing the temperature to be estimated to the nearest tenth of a degree. The thermometer on the right has marks every 0.1 °C. This scale permits estimation of the hundredths place.

The marks on the left thermometer are one degree apart, and we can see that the temperature lies between 24 °C and 25 °C. When reading a scale, we always record the last digit to the nearest tenth of the smallest scale division. Looking closely, therefore, we might estimate that the fluid column falls about 3/10 of the way between the marks for 24 and 25 degrees, so we can report the temperature to be 24.3 °C. However, it would be foolish to say that the temperature is *exactly* 24.3 °C. The last digit is only an estimate, and the left thermometer might be read as 24.2 °C by one observer or 24.4 °C by another. Because different observers might obtain values that differ by 0.1 °C, there is an uncertainty of ±0.1 °C in the measured temperature. We can express this by writing the temperature as 24.3 ± 0.1 °C.

The thermometer on the right has marks that are 1/10 of a degree apart, which allows us to estimate the temperature as 24.32 °C. In this case, we are estimating the hundredths place and the uncertainty is ±0.01 °C. We could write the temperature as 24.32 ± 0.01 °C. Notice that because the thermometer on the right is more finely graduated, we are able to obtain measurements with smaller uncertainties. We would have more confidence in temperatures read from the thermometer on the right in Figure 2.12 because it has more digits and a smaller amount of uncertainty. *The reliability of a measurement is indicated by the number of digits used to represent it.*

By convention in science, *all digits in a measurement up to and including the first estimated digit are recorded.* If a reading measured with the thermometer on the right seemed exactly on the 24 °C mark, we would record the temperature as 24.00 °C, not 24 °C, to show that the thermometer can be read to the nearest 1/100 of a degree.

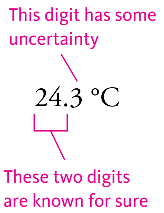
Modern laboratory instruments such as balances and meters often have digital displays. If you read the mass of a beaker on a digital balance as 65.23 grams, everyone else observing the same beaker will see the same display and obtain exactly the same reading. There seems to be no uncertainty, or estimation, in reading this type of scale. However, scientists agree that the uncertainty is ±1/2 of the last readable digit. Using this definition our digital reading may be written as 65.230 ± 0.005 grams.[5]

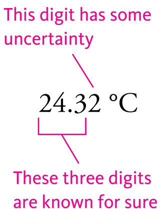
Significant Figures

The concepts discussed above are so important that we have special terminology to describe numbers that come from measurements.

> *Digits that result from a measurement such that only the digit farthest to the right is not known with certainty are called* **significant figures** (*or* **significant digits**).

The number of significant figures in a measurement is equal to the number of digits known for sure *plus* one that is estimated. Let's look at our two temperature measurements:


This digit has some uncertainty
24.3 °C
These two digits are known for sure


This digit has some uncertainty
24.32 °C
These three digits are known for sure

The first measurement, 24.3 °C, has three significant figures; the second, 24.32 °C, has four significant figures.

When Are Zeros Significant?

Usually, it is simple to determine the number of significant figures in a measurement; we just count the digits. Thus 3.25 has three significant figures and 56.205 has five of them. When zeros are in the middle of a number, imbedded zeros, they are always significant, but when they come at the beginning or the end of a number they sometimes cause confusion.

TOOLS

Counting significant figures

Trailing zeros are always counted as significant if the number has a decimal point. Thus, 4.500 m and 630.0 g have four significant figures each because the zeros would not be written unless those digits were known to be zeros.

Zeros to the left of the first nonzero digit, called leading zeros, are never counted as significant. For instance, a length of 2.3 mm is the same as 0.0023 m. Since we are dealing with the same measured value, its number of significant figures cannot change when we change the units. Both quantities have two significant figures.

Zeros on the end of a number that does not have a decimal point are assumed not to be significant. For example, suppose you were told that a protest march was attended by 45,000 people. If this was just a rough estimate, it might be uncertain by as much as several thousand, in which case the value 45,000 represents just two significant figures, since the "5" is the uncertain digit. None of the zeros would then count as significant figures. On the other hand, suppose the protesters were carefully counted using an aerial photograph, so that the count could be reported to be 45,000—give or take about 100 people. In this case, the value represents 45,000 ± 100 protesters and contains three significant figures, with the uncertain digit being the zero in the hundreds place. Thus, a simple statement such as "there were 45,000 people attending the march" is ambiguous. We can't tell how many significant digits the number has from the number alone. We can be sure that the nonzero digits are significant, though. The best we can do is to say "45,000 has *at least* two significant figures."

---

[5] Some instructors may wish to maintain a uniform procedure of assigning an uncertainty of ±1 in the last readable digit for both analog and digital scale readings.

We can avoid this confusion by using **scientific notation** when we report a measurement. For example, if we want to report the number of protesters as 45,000 give or take a thousand, we can write the rough estimate as 4.5×10^4. The 4.5 shows the number of significant figures and the 10^4 tells us the location of the decimal. The value obtained from the aerial photograph count, on the other hand, can be expressed as 4.50×10^4. This time the 4.50 shows three significant figures and an uncertainty of $\pm 0.01 \times 10^4$ or ±100 people.

Accuracy and Precision

Two words often used in reference to measurements are accuracy and precision. **Accuracy** *refers to how close a measurement is to the true or the accepted true value.* **Precision** *refers to how close repeated measurements come to their average.* Notice that the two terms are not synonyms, because the average doesn't always correspond to the true or correct value. A practical example of how accuracy and precision differ is illustrated in Figure 2.13.

For measurements to be **accurate**, the measuring device must be carefully calibrated (adjusted) with a standard reference so it gives correct readings. For example, to calibrate an electronic balance, a known reference mass is placed on the balance and a calibration routine within the balance is initiated. Once calibrated, the balance will give accurate readings, the accuracy of which is determined by the quality of the standard mass used. Standard reference masses, often "traceable" to the international prototype kilogram in Paris, can be purchased from scientific supply companies.

Precision refers to how closely repeated measurements of the same quantity come to each other. In general, the smaller the uncertainty (i.e., the "plus or minus" part of the measurement), the more precise the measurement. This translates as: *The more significant figures in a measured quantity, the more precise the measurement.*

We usually assume that a very precise measurement is also of high accuracy. We can be wrong, however, if our instruments are improperly calibrated. For example, the improperly marked ruler in Figure 2.14 might yield measurements that vary by a hundredth of a centimeter (±0.01 cm), but all the measurements would be too large by 1 cm—a case of good precision but poor accuracy.

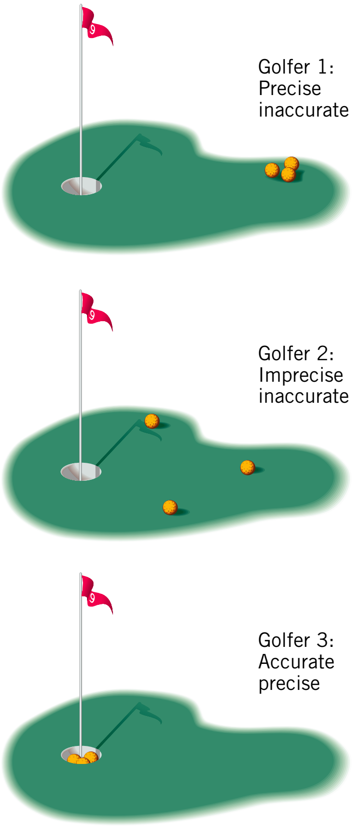


Figure 2.13 | **The difference between precision and accuracy in the game of golf.** Golfer 1 hits shots that are precise (because they are tightly grouped), but the accuracy is poor because the balls are not near the target (the "true" value). Golfer 2 needs help. His shots are neither precise nor accurate. Golfer 3 wins the prize with shots that are precise (tightly grouped) and accurate (in the hole).

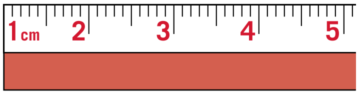

1 cm
2
3
4
5
How accurate would measurements be with this ruler?

Figure 2.14 | **An improperly marked ruler.** This improperly marked ruler will yield measurements that are each wrong by one whole unit. The measurements might be precise, but the accuracy would be very poor.

Significant Figures in Calculations

When several measurements are obtained in an experiment they are usually combined in some way to calculate a desired quantity. For example, to determine the area of a rectangular carpet we require two measurements, length and width, which are then multiplied to give the answer we want. To get some idea of how precise the area really is, we need a way to take into account the precision of the various values used in the calculation. To make sure this happens, we follow certain rules according to the kinds of arithmetic being performed.

Significant figures: multiplication and division

Multiplication and Division

For multiplication and division, the number of significant figures in the answer should not be greater than the number of significant figures in the least precise measurement. The least precise measurement is the number with the fewest significant figures. Let's look at a typical problem involving some measured quantities.

$$\frac{\overset{\text{3 sig. figures}}{3.14} \times \overset{\text{4 sig. figures}}{2.751}}{\underset{\text{2 sig. figures}}{0.64}} = 13$$

The result displayed on a calculator[6] is 13.49709375. However, the least precise factor, 0.64, has only two significant figures, so the answer should have only two. The correct answer, 13, is obtained by rounding off the calculator answer.[7] When we multiply and divide measurements, the units of those measurements are multiplied and divided in the same way as the numbers.

Significant figures: addition and subtraction

Addition and Subtraction

For addition and subtraction, the answer should have the same number of decimal places as the quantity with the fewest number of decimal places. As an example, consider the following addition of measured quantities.

$$\begin{array}{r l} 3.247 & \\ 41.36 & \\ +125.2 & \longleftarrow \text{(This number has only 1 decimal place.)} \\ \hline 169.8 & \longleftarrow \text{(This answer has been rounded to 1 decimal place.)} \end{array}$$

In this calculation, the digits beneath the 6 and the 7 are unknown; they could be anything. (They're not necessarily zeros because if we *knew* they were zeros, then zeros would have been written there.) Adding an unknown digit to the 6 or 7 will give an answer that's also unknown, so for this sum we are not justified in writing digits in the second and third places after the decimal point. Therefore, we round the answer to the nearest tenth. We must also recall that we can only add and subtract numbers that have identical units, and the answer will have the same units.

Significant figures: exact numbers

Exact Numbers

Numbers that come from definitions, such as 12 in. = 1 ft, and those that come from a direct count, such as the number of people in a small room, have no uncertainty, and we can assume that they have an infinite number of significant figures. Therefore, exact numbers do not affect the number of significant figures in multiplication or division calculations.

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[6] Calculators usually give too many significant figures. An exception is when the answer has zeros at the right that are significant figures. For example, an answer of 1.200 is displayed on most calculators as 1.2. If the zeros belong in the answer, be sure to write them down.

[7] When we wish to round off a number at a certain point, we simply drop the digits that follow if the first of them is less than 5. Thus, 8.1634 rounds to 8.16 if we wish to have only two decimal places. If the first digit after the point of round off is larger than 5, or if it is 5 followed by other nonzero digits, then we add 1 to the preceding digit. Thus 8.167 and 8.1653 both round to 8.17. Finally, when the digit after the point of round off is a 5 and no nonzero digits follow the 5, then we drop the 5 if the preceding digit is even and add 1 if it is odd. Thus, 8.165 rounds to 8.16 and 8.17500 rounds to 8.18.

Practice Exercises

2.5 | Perform the following calculations involving measurements and round the results so they have the correct number of significant figures and proper units. (*Hint:* Apply the rules for significant figures described in this section, and keep in mind that units behave as numbers do in calculations.)

(a) $21.0233\text{ g} + 21.0\text{ g}$
(b) $10.0324\text{ g} \div 11.7\text{ mL}$
(c) $\dfrac{14.25\text{ cm} \times 12.334\text{ cm}}{(2.223\text{ cm} - 1.04\text{ cm})}$

2.6 | Perform the following calculations involving measurements and round the results so that they are written to the correct number of significant figures and have the correct units.

(a) $32.02\text{ mL} - 2.0\text{ mL}$
(b) $54.183\text{ g} - 0.0278\text{ g}$
(c) $10.0\text{ g} + 1.03\text{ g} + 0.243\text{ g}$
(d) $43.4\text{ in.} \times \dfrac{1\text{ ft}}{12\text{ in.}}$
(e) $\dfrac{1.03\text{ m} \times 2.074\text{ m} \times 3.9\text{ m}}{12.46\text{ m} + 4.778\text{ m}}$

2.4 | Dimensional Analysis

Earlier we mentioned that for numerical problems we often do not have a specific equation to solve; instead, all we need to do is convert one set of units to another. After analyzing the problem and assembling the necessary information to solve it, scientists usually use a technique commonly called **dimensional analysis** (also called the **factor-label method**) to help them perform the correct arithmetic. As you will see, often this method also helps in analyzing the problem and selecting the tools needed to solve it.

Conversion Factors

In dimensional analysis we treat a numerical problem as one involving a conversion of units (the dimensions) from one kind to another. To do this we use one or more *conversion factors* to change the units of the given quantity to the units of the answer.

$$(\text{given quantity}) \times (\text{conversion factor}) = (\text{desired quantity})$$

A **conversion factor** *is a fraction formed from a* valid *equality or equivalence between units and is used to switch from one system of measurement and units to another.* To illustrate, suppose we want to express a person's height of 72.0 inches in centimeters. To do this we need the relationship between the inch and the centimeter. We can obtain this from Table 2.3:

■ To construct a valid conversion factor, the relationship between the units must be true. For example, the statement 3 ft = 41 in. is false. Although you might make a conversion factor out of it, any answers you would calculate are sure to be wrong. Correct answers require correct relationships between units.

$$2.54\text{ cm} = 1\text{ in. (exactly)} \qquad \textbf{(2.4)}$$

If we divide both sides of this equation by 1 in., we obtain a conversion factor.

$$\frac{2.54\text{ cm}}{1\text{ in.}} = \frac{1\,\cancel{\text{in.}}}{1\,\cancel{\text{in.}}} = 1$$

Notice that we have canceled the units from both the numerator and denominator of the center fraction, leaving the first fraction equaling 1. As mentioned earlier, *units behave* *just as numbers do in mathematical operations*; this is a key part of dimensional analysis. Let's see what happens if we multiply 72.0 inches, the height that we mentioned, by this fraction.

■ The relationship between the inch and the centimeter is exact, so that the numbers in 1 in. = 2.54 cm have an infinite number of significant figures.

$$72.0\ \cancel{\text{in.}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in.}}} = 183\ \text{cm}$$

$$(\text{given quantity}) \times (\text{conversion factor}) = (\text{desired quantity})$$

Because we have multiplied 72.0 in. by something that is equal to 1, we know we haven't changed the magnitude of the person's height. We have, however, changed the units. Notice that we have canceled the unit inches. The only unit left is centimeters, which is the unit we want for the answer. The result, therefore, is the person's height in centimeters.

One of the benefits of dimensional analysis is that it often lets you know when you have done the *wrong* arithmetic. From the relationship in Equation 2.4, we can actually construct two conversion factors:

$$\frac{2.54\ \text{cm}}{1\ \text{in.}} \quad \text{and} \quad \frac{1\ \text{in.}}{2.54\ \text{cm}}$$

We used the first one correctly, but what would have happened if we had used the second by mistake?

$$72.0\ \text{in.} \times \frac{1\ \text{in.}}{2.54\ \text{cm}} = 28.3\ \text{in.}^2/\text{cm}$$

In this case, none of the units cancel. We get units of in.^{2}/cm because inches times inches is inches squared. Even though our calculator may be very good at arithmetic, we've got the wrong answer. *Dimensional analysis lets us know we have the wrong answer because the units are wrong!*

We will use dimensional analysis extensively throughout this book to aid us in setting up the proper arithmetic in problems. In fact, we will see that in many cases this approach also helps us assemble the information we need to solve a problem.

There is a general strategy for all problems that involve a conversion. We always start with a given piece of data along with its units. Then we write down the desired units that we want the answer to have. This gives us the start and end points of our calculation. Then, all we need to do is find the correct conversion factors that will lead us from one set of units to the next. Sometimes this will require one conversion factor, other times it may take two or three (or more!) to complete the conversion. The next examples illustrate this process.

Example 2.3
Dimensional Analysis Applied to Metric Prefixes

Convert 3.25 m to millimeters (mm).

■ **Analysis:** We are asked to convert a number with meter units to another number that has millimeter units. This is a problem that involves conversion of metric prefixes.

■ **Assembling the Tools:** To solve this problem, our tool will be a conversion factor that relates the unit meter to the unit millimeter. From Table 2.4, the table of decimal multipliers, the prefix "milli" means "$\times\ 10^{-3}$," so we can write

$$1\ \text{mm} = 10^{-3}\ \text{m}$$

Notice that this relationship connects the units given to the units desired.

We now have all the information we need to solve the problem.

■ **Solution:** Based on the general strategy for conversion problems, let's write the given quantity (with its units) on the left and the *units* of the desired answer on the right.

$$3.25\ \text{m} = ?\ \text{mm}$$

From the relationship above, we can form two conversion factors.

$$\frac{1\ \text{mm}}{10^{-3}\ \text{m}} \quad \text{and} \quad \frac{10^{-3}\ \text{m}}{1\ \text{mm}}$$

We know we have to cancel the unit meter, so we need to multiply by a conversion factor with this unit in the denominator. Therefore, we select the one on the left as our tool. This gives

$$3.25\ \cancel{\text{m}} \times \frac{1\ \text{mm}}{10^{-3}\ \cancel{\text{m}}} = 3.25 \times 10^{3}\ \text{mm}$$

Notice that we have expressed the answer to three significant figures because that is how many there are in the given quantity, 3.25 m. The equality that relates meters and millimeters involves exact numbers because it is a definition.

■ **Is the Answer Reasonable?** We know that millimeters are much smaller than meters, so 3.25 m must represent a lot of millimeters. We also know that conversions between prefixes will not change the 3.25 part of our number, just the power of 10. Our answer, therefore, makes sense.

Example 2.4

Using Dimensional Analysis

A liter, which is slightly larger than a quart, is defined as 1 cubic decimeter (1 dm^3). How many liters are there in exactly 1 cubic meter (1 m^3)?

■ **Analysis:** Let's begin once again by stating the problem in equation form.

$$1\ \text{m}^3 = ?\ \text{L}$$

Now we will use this to identify what relationships we will need to solve the problem. We don't have any direct conversions between cubic meters and liters. There was, however, a definition of the liter in terms of base metric units that we can combine with metric prefixes to do the job.

■ **Assembling the Tools:** The relationship between liters and cubic decimeters was given in Equation 2.1,

$$1\ \text{L} = 1\ \text{dm}^3$$

From the table of decimal multipliers, we also know the relationship between decimeters and meters,

$$1\ \text{dm} = 0.1\ \text{m}$$

but we need a relationship between cubic units. Since units undergo the same kinds of operations numbers do, we simply cube each side of this equation (being careful to cube *both* the numbers and the units).

$$(1\ \text{dm})^3 = (0.1\ \text{m})^3$$

$$1\ \text{dm}^3 = 0.001\ \text{m}^3 \qquad \textbf{(2.5)}$$

Notice how Equations 2.5 and 2.1 provide a path from the given units to those we seek. Such a path is always a necessary condition when we work with dimensional analysis.

$$\text{m}^3 \xrightarrow[\text{Equation 2.5}]{} \text{dm}^3 \xrightarrow{\text{Equation 2.1}} \text{L}$$

Now we are ready to solve the problem.

■ **Solution:** The first step is to eliminate the units m^3. We use Equation 2.5.

$$1\ \cancel{\text{m}^3} \times \frac{1\ \text{dm}^3}{0.001\ \cancel{\text{m}^3}} = 1000\ \text{dm}^3$$

Then we use Equation 2.1 to take us from dm^3 to L.

$$1000\ \cancel{\text{dm}^3} \times \frac{1\ \text{L}}{1\ \cancel{\text{dm}^3}} = 1000\ \text{L}$$

Thus, $1\ \text{m}^3 = 1000\ \text{L}$.

Usually, when a problem involves the use of two or more conversion factors, they can be "strung together" in a "chain calculation" to avoid having to compute intermediate results. For example, this problem can be set up as follows.

$$1\ \cancel{\text{m}^3} \times \frac{1\ \cancel{\text{dm}^3}}{0.001\ \cancel{\text{m}^3}} \times \frac{1\ \text{L}}{1\ \cancel{\text{dm}^3}} = 1000\ \text{L}$$

Since all of our conversion factors involve exact numbers and we were given exactly one cubic meter, our answer is an exact number also.

■ **Is the Answer Reasonable?** One liter is about a quart. A cubic meter is about a cubic yard. Therefore, we expect a large number of liters in a cubic meter, so our answer seems reasonable. (Notice here that in our analysis we have approximated the quantities in the calculation in units of quarts and cubic yards, which may be more familiar than liters and m^3 if you've been raised in the United States. We get a feel for the approximate magnitude of the answer using our familiar units and then relate this to the actual units of the problem.)

Example 2.5
Applying Dimensional Analysis to Non-SI Units

Some mountain climbers are susceptible to high altitude pulmonary edema (HAPE), a life-threatening condition that causes fluid retention in the lungs. It can develop when a person climbs rapidly to heights greater than 2.5×10^3 meters (2,500 m). What is this distance expressed in feet?

■ **Analysis:** The problem can be stated as

$$2.5 \times 10^3\ \text{m} = ?\ \text{ft}$$

We are converting a metric unit of length (the meter) into an English unit of length (the foot). Since Table 2.3 does not have a relationship between feet and meters this is obviously not a one-step conversion, let's develop a sequence of conversions by looking at the units we can convert. One sequence may be:

$$2.5 \times 10^3\ \text{m} \longrightarrow \text{centimeters} \longrightarrow \text{inches} \longrightarrow \text{feet}$$

and if we consult the inside back cover of this book we find the conversion factor 1 yard = 0.9144 meters, so another multistep sequence could be

$$2.5 \times 10^3\ \text{m} \longrightarrow \text{yards} \longrightarrow \text{feet}$$

We will choose the first sequence for this example.

Assembling the Tools: The tools we will need can be found by looking in the appropriate tables as shown.

$$1\text{ cm} = 10^{-2}\text{ m} \quad (\text{from Table 2.4})$$
$$1\text{ in.} = 2.54\text{ cm} \quad (\text{from Table 2.3})$$
$$1\text{ ft} = 12.\text{ in.}$$

Solution: Now we apply dimensional analysis by following our planned sequence of eliminating unwanted units to bring us to the units of the answer.

$$2.5\times10^{3}\ \cancel{\text{m}} \times \frac{1\ \cancel{\text{cm}}}{10^{-2}\ \cancel{\text{m}}} \times \frac{1\ \cancel{\text{in.}}}{2.54\ \cancel{\text{cm}}} \times \frac{1\text{ ft}}{12\ \cancel{\text{in.}}} = 8.2\times10^{3}\text{ ft}$$

Notice that if we were to stop after the first conversion factor, the units of the answer would be centimeters. If we stop after the second, the units would be inches, and after the third we get feet—the units we want. This time the answer has been rounded to two significant figures because that's how many there were in the measured distance. Notice that the numbers 12 and 2.54 do not affect the number of significant figures in the answer because they are exact numbers derived from definitions.

As suggested in the analysis, this is not the only way we could have solved this problem. Other sets of conversion factors could have been chosen. For example, we could have followed the second sequence of conversions and used: 1 yd = 0.9144 m and 3 ft = 1 yd. Then the problem would have been set up as follows:

$$2500\ \cancel{\text{m}} \times \frac{1\ \cancel{\text{yd}}}{0.9144\ \cancel{\text{m}}} \times \frac{3\text{ ft}}{1\ \cancel{\text{yd}}} = 8200\text{ ft} \quad (\text{rounded correctly})$$

Many problems that you meet, just like this one, have more than one path to the answer. There isn't necessarily any *one* correct way to set up the solution. *The important thing is for you to be able to reason your way through a problem and find some set of relationships that can take you from the given information to the answer.* Dimensional analysis can help you search for these relationships if you keep in mind the units that must be eliminated by cancellation.

Is the Answer Reasonable? Let's do some approximate arithmetic to get a feel for the size of the answer. A meter is slightly longer than a yard, so let's approximate the given distance, 2500 m, as 2500 yd. In 2500 yd, there are 3 × 2500 = 7500 ft. Since the meter is a bit longer than a yard, our answer should be a bit longer than 7500 ft, so the answer of 8200 ft seems to be reasonable.

Practice Exercises

2.7 | Use dimensional analysis to convert an area of 124 ft^2 to square meters. (*Hint:* What relationships would be required to convert feet to meters?)

2.8 | Use dimensional analysis to perform the following conversions: (a) 3.00 yd to inches, (b) 1.25 km to centimeters, (c) 3.27 mm to feet, (d) 20.2 miles/gallon to kilometers/liter.

Equivalencies

Up to now we've constructed conversion factors from relationships that are literally equalities. We can also make conversion factors from expressions that show how one thing is *equivalent* to another. For instance, if you buy a pair of sneakers for \$75, we can say you converted \$75 into a pair of sneakers or \$75 is equivalent to a pair of sneakers. We would write this as

$$\$75 \Leftrightarrow 1\text{ pair of sneakers}$$

where the symbol ⇔ is read as "is equivalent to." Mathematically, this equivalence sign works the same as an equal sign and we can construct two conversion factors as

$$\frac{\$75}{1\text{ pair of sneakers}} \quad \text{or} \quad \frac{1\text{ pair of sneakers}}{\$75}$$

that allow us to convert from sneakers to dollars or from dollars to sneakers.

Let's now look at a problem that has a direct relationship to the chemistry we are studying. In Chapter 1 we learned that Dalton's atomic theory predicted the **law of multiple proportions**. The basic idea of this law is that two elements often can form two different compounds. If we take samples of the two compounds so that the mass of one of the elements in those samples is the same, then the mass ratio of the other element in the two samples will be a ratio of small whole numbers. It is experimentally difficult, or very inconvenient, to obtain sample masses suggested above. However, if we analyze each sample for the elemental composition, we can perform a calculation that will illustrate the law of multiple proportions. Let's see how this works by working through Example 2.6.

Example 2.6

Applying the Law of Multiple Proportions

Titanium forms two different compounds with bromine. In compound A we find that 4.787 g of Ti are combined with 15.98 g of bromine. In compound B we find that 6.000 g of Ti are combined with 40.06 g of bromine. Determine whether these data support the law of multiple proportions.

■ **Analysis:** We need to set up a situation where we have the same mass of one of the elements in samples of the two compounds, and then take the corresponding ratio of the masses of the other element. For this example, let's assume that we select samples so that we have 6.000 g of Ti in compound A and 6.000 g of Ti in compound B.

■ **Assembling the Tools:** We will need to use the law of definite proportions to relate the amounts in the two compounds. We set up the two equivalencies we may need using the composition of each substance:

$$\text{In compound A:} \quad 4.787 \text{ g Ti} \Leftrightarrow 15.98 \text{ g Br}$$
$$\text{In compound B:} \quad 6.000 \text{ g Ti} \Leftrightarrow 40.06 \text{ g Br}$$

■ **Solution:** We decided in the Analysis to compare the two compounds when samples of them each had 6.000 g of titanium. Our initial data shows that compound B was given to us with 6.000 g of Ti. However, the sample of compound A had only 4.787 g of Ti. We need to determine how much bromine will be present if a sample of compound A has 6.000 g of Ti. To do this we convert 6.000 g of Ti in compound A to the equivalent mass of Br using the conversion factor from the compound A data. We start by writing this question as an equation,

■ The equivalence symbol, ⇔, acts just like an equal sign.

$$6.000 \text{ g Ti} \Leftrightarrow ? \text{ g Br} \quad \text{(in compound A)}$$

then we apply the conversion factor for compound A to get the solution,

$$6.000 \cancel{\text{g Ti}} \times \frac{15.98 \text{ g Br}}{4.787 \cancel{\text{g Ti}}} = 20.03 \text{ g Br}$$

We now know that 6.000 g of Ti combine with 20.03 g of Br in compound A, and we were given information that 6.000 g of Ti combine with 40.06 g of Br in compound B. Taking the ratio of bromine in the two compounds, we get

■ A mathematically equivalent method is to take the ratio of the masses of the elements in the two compounds, ratio_a and ratio_b. Then take the ratio of those ratios, $\frac{\text{ratio}_a}{\text{ratio}_b}$, to obtain the ratio of small whole numbers.

$$\frac{20.03}{40.06} = \frac{1}{2} \quad \text{or} \quad \frac{40.06}{20.03} = \frac{2}{1}$$

Either of these is a ratio of small whole numbers. This verifies the law of multiple proportions.

■ **Is the Answer Reasonable?** The fact that our ratio gave us whole numbers is usually sufficient to consider the answer reasonable.

2.5 | Density and Specific Gravity

In our earlier discussion of properties we noted that intensive properties are useful for identifying substances. One of the interesting things about extensive properties is that if you take the ratio of two of them, the resulting quantity is usually independent of sample size. In effect, the sample size cancels out and the calculated quantity becomes an intensive property. A useful property obtained this way is **density**, *which is defined as the ratio of an object's mass to its volume*. Using the symbols d for density, m for mass, and V for volume, we can express this mathematically as

$$d = \frac{m}{V} \tag{2.6}$$

TOOLS
Density

Notice that to determine an object's density we make two measurements, mass and volume.

Example 2.7
Calculating Density

A sample of blood completely fills an 8.20 cm^3 vial. The empty vial has a mass of 10.30 g. The vial has a mass of 18.91 g after being filled with blood. What is the density of blood in units of g/cm^3?

■ **Analysis:** This problem asks you to connect the mass and volume of blood with its density. We are given the volume of the blood but not its mass. However, we are given information that allows us to calculate the mass. Once we have the mass and volume, we can use the definition of density to solve the problem.

■ **Assembling the Tools:** The law of conservation of mass is one tool we need. It can be stated as follows:

$$\text{mass of full vial} = \text{mass of empty vial} + \text{mass of blood}$$

The other tool needed is the definition of density, given by Equation 2.6.

■ **Solution:** The mass of the blood is the difference between the masses of the full and empty vials:

$$\text{mass of blood} = 18.91\text{ g} - 10.30\text{ g} = 8.61\text{ g}$$

To determine the density we simply take the ratio of mass to volume.

$$\text{density} = \frac{m}{V} = \frac{8.61\text{ g}}{8.20\text{ cm}^3} = 1.05\text{ g cm}^{-3}$$

This could also be written as density = 1.05 g/mL, because 1 cm^3 = 1 mL.

■ **Is the Answer Reasonable?** First, the answer has the correct units, so that's encouraging. In the calculation we are dividing 8.61 by a number that is slightly smaller, 8.20. The answer should be slightly larger than one, which it is, so a density of 1.05 g/cm^3 seems reasonable.

Each pure substance has its own characteristic density (Table 2.5). Gold, for instance, is much more dense than iron. Each cubic centimeter of gold has a mass of 19.3 g, so its density is 19.3 g/cm^3. The same volume of iron will weigh 7.86 g and have a density of 7.86 g/cm^3. By comparison, the density of water is 1.00 g/cm^3, and the density of air at room temperature is about 0.0012 g/cm^3.

■ There is more mass in 1 cm^3 of gold than in 1 cm^3 of iron.

Table 2.5 Densities of Some Common Substances in g/cm^3 at Room Temperature

Water	1.00
Aluminum	2.70
Iron	7.86
Silver	10.5
Gold	19.3
Glass	2.2
Air	0.0012

Table 2.6 Density of Water as a Function of Temperature

Temperature (°C)	Density (g/cm^3)
10	0.999700
15	0.999099
20	0.998203
25	0.997044
30	0.995646
50	0.988036
100	0.958364

Most substances, such as the fluid in the bulb of a thermometer, expand slightly when they are heated, so the amount of matter packed into each cubic centimeter is less. Therefore, density usually decreases slightly with increasing temperature.[8] For solids and liquids the size of this change is small, as you can see from the data for water in Table 2.6. When only two or three significant figures are required, we can often ignore the variation of density with temperature.

■ Although the density of water varies slightly with temperature, it is very close to 1.00 g/cm^3 when the temperature is close to room temperature, 25 °C.

Density as a Conversion Factor

A useful property of density is that it provides a way to convert between the mass and volume of a substance. It defines a relationship, which we previously called an equivalence, between the amount of mass and its volume. For instance, the density of gold (19.3 g/cm^3) tells us that 19.3 g of the metal is equivalent to a volume of 1.00 cm^3. We express this relationship symbolically as

$$19.3 \text{ g gold} \Leftrightarrow 1.00 \text{ cm}^3 \text{ gold}$$

where we have used the symbol ⇔ to mean "is equivalent to." In setting up calculations for dimensional analysis, an equivalence can be used to construct conversion factors just as equalities can. From the equivalence we have just written, we can form two conversion factors:

$$\frac{19.3 \text{ g gold}}{1.00 \text{ cm}^3 \text{ gold}} \quad \text{and} \quad \frac{1.00 \text{ cm}^3 \text{ gold}}{19.3 \text{ g gold}}$$

The following example illustrates how we use density in calculations.

Example 2.8
Calculations Using Density

Seawater has a density of about 1.03 g/mL. (a) What mass of seawater would fill a sampling vessel to a volume of 225 mL? (b) What is the volume, in milliliters, of 45.0 g of seawater?

■ **Analysis:** For both parts of this problem, we are relating the mass of a material to its volume. We have recently found that density provides a direct relationship between mass and volume, so this should be a one-step conversion.

---

[8] Liquid water behaves oddly. Its maximum density is at 4 °C, so when water at 0 °C is warmed, its density increases until the temperature reaches 4 °C. As the temperature is increased further, the density of water gradually decreases.

Assembling the Tools: Density, Equation 2.6, is the only tool that we need to convert between these two quantities. We write the equivalence for this problem as

$$1.03 \text{ g seawater} \Leftrightarrow 1.00 \text{ mL seawater}$$

From this relationship we can construct two conversion factors. These will be the tools we use to obtain the answers.

$$\frac{1.03 \text{ g seawater}}{1.00 \text{ mL seawater}} \quad \text{and} \quad \frac{1.00 \text{ mL seawater}}{1.03 \text{ g seawater}}$$

Solution to (a): The question can be restated as:

$$225 \text{ mL seawater} \Leftrightarrow ? \text{ g seawater}$$

We need to eliminate the unit *mL seawater*, so we choose the conversion factor on the left as our tool.

$$225 \cancel{\text{ mL seawater}} \times \frac{1.03 \text{ g seawater}}{1.00 \cancel{\text{ mL seawater}}} = 232 \text{ g seawater}$$

Thus, 225 mL of seawater has a mass of 232 g.

Solution to (b): The question is: 45.0 g seawater ⇔ ? mL seawater. This time we need to eliminate the unit *g seawater*, so we use the conversion factor on the right as our tool.

$$45.0 \cancel{\text{ g seawater}} \times \frac{1.00 \text{ mL seawater}}{1.03 \cancel{\text{ g seawater}}} = 43.7 \text{ mL seawater}$$

Thus, 45.0 g of seawater has a volume of 43.7 mL.

Are the Answers Reasonable? Notice that the density tells us that 1 mL of seawater has a mass of slightly more than 1 g. Thus, for part (a), we might expect that 225 mL of seawater should have a mass slightly more than 225 g. Our answer, 232 g, is reasonable. For part (b), 45 g of seawater should have a volume not too far from 45 mL, so our answer of 43.7 mL is the right size.

Practice Exercises

2.9 | A gold-colored metal object has a mass of 365 g and a volume of 22.12 cm^3. Is the object composed of pure gold? (*Hint:* How does the density of the object compare with that of pure gold?)

2.10 | A certain metal alloy has a density of 12.6 g/cm^3. How many pounds would 0.822 ft^3 of this alloy weigh? (*Hint:* What is the density of this alloy in units of lb/ft^3?)

2.11 | An ocean-dwelling dinosaur was estimated to have had a body volume of $1.38 \times 10^6 \text{ cm}^3$. The animal's mass when alive was estimated at 1.24×10^3 kg. What was its density?

2.12 | The density of diamond is 3.52 g/cm^3. What is the volume in cubic centimeters of a 1.125 carat diamond, which has a mass of 225 mg?

Specific Gravity

Density is the ratio of mass to volume of a substance. We used units of grams for the mass and cubic centimeters for the volume in our examples. This is entirely reasonable since most liquids and solids have densities between 0.5 and 20 g/cm^3. There are many different units for mass. Kilograms, grams, micrograms, pounds, ounces, and drams come to mind, and there are undoubtedly more. Volume also has many possible units: cm^3, liters, ounces, gallons, and so on. From those listed, there are 30 different possible ratios of mass and volume units for density. Many professions have their own preferred units for density and

CHEMISTRY OUTSIDE THE CLASSROOM 2.1

Density and Wine

(Steve Hyde/Flicker/Getty Images, Inc)

Density, or specific gravity, is one of the basic measurements in the wine making process. The essential chemical reaction is that yeast cells feed on the sugars in the grape juice and one of the products is ethanol (ethyl alcohol) and the other product is carbon dioxide. This is the fermentation process. The two main sugars in grapes are glucose and fructose. The fermentation reaction for these sugars are

$$C_6H_{12}O_6(aq) \longrightarrow 2CH_3CH_2OH\ (aq) + 2CO_2(g)$$

If there is too little sugar the amount of alcohol in the product will be low. Too much sugar will result in a maximum amount of alcohol, about 13%, but there will be leftover sugar. Wines that are sweet with leftover sugars or low in alcohol are not highly regarded.

To make high quality wines the natural sugar content of the grapes is monitored carefully, toward the end of the growing season. When the sugar content reaches the optimum level the grapes are harvested, crushed and pressed to start the fermentation process.

A very quick way to determine the sugar content of the grapes is to determine the density of the juice. The higher the density, the higher the sugar content. Vintners use a simple device called a hydrometer. The hydrometer is a weighted glass bulb with a graduated stem. Placed in a liquid and given a slight spin the hydrometer will stay centered in the graduated cylinder and sink to a level that is proportional to the density. After the density is read from the hydrometer scale, the vintner consults a calibration chart to find the corresponding sugar content.

Once the fermentation ends, the alcohol content must also be determined. Again, this is done by measuring the density. To do this, a sample of wine is distilled by heating it to boiling and condensing the alcohol and water that are vaporized. When the required amount of liquid has been condensed, its density is determined using another hydrometer. Using calibration tables, the density reading is converted into the percentage alcohol.

ml
C20°C
120
135
150
165
Hydrometer used for measuring sugar content in crushed grapes before fermentation. *(WarrenMcConnaughie/Alamy)*

130
120
110
100
90
50
40
30
20
10
Hydrometer used for measuring alcohol content in a distilled wine sample after fermentation. *(Paul Silverman/Fundamental Photographs)*

would like to see them tabulated in reference books. This would result in each substance having 30 different densities listed in tables. Imagine the confusion, and the possibility of repeating the Mars Orbiter mistake becomes very probable.

The concept of *specific gravity solves this problem.* The **specific gravity** for a substance is simply the density of that substance divided by the density of water. The units for the two densities must be the same so that specific gravity will be a *dimensionless number*. In addition other experimental conditions, such as temperature, for determining the two densities must be the same.

TOOLS
Specific gravity

$$\text{specific gravity} = \frac{\text{density of substance}}{\text{density of water}} \tag{2.7}$$

To use the specific gravity, the scientist simply selects the specific gravity of the desired substance and then multiplies it by the density of water that has the units desired. Now we can have a relatively compact table that lists the specific gravity for our chemical substances and then a second short table of the density of water, perhaps in the 30 different units suggested above.

Example 2.9
Using Specific Gravity

Concentrated sulfuric acid is sold in bottles with a label that states that the specific gravity at 25 °C is 1.84. The density of water at 25 °C is 62.4 pounds per cubic foot. How many cubic feet of sulfuric acid will weigh 55.5 pounds?

■ **Analysis:** We rewrite the question as an equation,

$$55.5 \text{ lb sulfuric acid} = ?\ \text{ft}^3 \text{ sulfuric acid}$$

We saw how to use density to convert mass to volume. The specific gravity needs to be converted to density units, preferably pounds and cubic feet so that this can be a one-step conversion.

■ **Assembling the Tools:** We have Equation 2.7 defining specific gravity. We know two of the variables, and simple algebra will allow us to calculate the density of sulfuric acid. We will then use the density as a conversion factor as we did in Example 2.7.

■ **Solution:** Rearranging the specific gravity equation we get

$$\text{density sulfuric acid} = (\text{specific gravity}) \times (\text{density of water}) = 1.84 \times 62.4 \text{ lb/ft}^3$$

$$\text{density sulfuric acid} = 114.8 \text{ lb/ft}^3$$

We now perform the conversion with the conversion factor from the density,

$$55.5 \text{ lb sulfuric acid} \times \frac{1 \text{ ft}^3}{114.8 \text{ lb}} = 0.483 \text{ ft}^3$$

■ **Is the Answer Reasonable?** We can do some quick estimations. The density seems correct: since the specific gravity is approximately 2 and the density of water is approximately 60, an answer near 120 is expected. For the second part, we see that 114 is about twice the size of 55.5 so we expect an answer of about 0.5. Our answer is very close to that, suggesting that our answers are reasonable.

Importance of Reliable Measurements

We saw earlier that substances can be identified by their properties. If we are to rely on properties such as density for identification of substances, it is very important that our measurements be reliable. We must have some idea of what the measurements' accuracy and precision are.

The importance of accuracy is obvious. If we have no confidence that our measured values are close to the true values, we certainly cannot trust any conclusions that are based on the data we have collected.

Precision of measurements can be equally important. For example, suppose we had a gold wedding ring and we wanted to determine whether or not the gold was 24 carat. We could determine the mass of the ring, and then its volume, and compute the density of the ring. We could then compare our experimental density with the density of 24 carat gold (which is 19.3 g/mL). Suppose the ring had a volume of 1.0 mL and the ring had a mass of 18 g, as measured using a graduated cup measure and a kitchen scale. The density of the ring would then be 18 g/mL, to the correct number of significant figures. Could we conclude that the ring was made of 24 carat gold? We know the density to only two significant figures, and we compare it to the tabulated densities, also rounded to two significant figures. The experimental density could be as low as 17 g/mL or as high as 19 g/mL, which means the ring could be 24 carat gold—or it could be 22 carat gold (which has a density of around 17.7 to 17.8 g/mL) or maybe even 18 carat gold (which has a density up to 16.9 g/mL).

■ The carat system for gold states that pure gold is referred to as 24 carat gold. Gold that is 50% gold by mass will be 12 carat. Gold that is less than 24 carats is usually alloyed with cheaper metals such as silver and copper.

Suppose we now measure the mass of the ring with a laboratory balance capable of measurements to the nearest ±0.001 g and obtain a mass of 18.153 g. We measure the volume using volumetric glassware and find a volume of 1.03 mL. The density is 17.6 g/mL to the correct number of significant figures. The difference between this density and the density of 24 carat gold is 19.3 g/mL − 17.6 g/mL = 1.7 g/mL. This is considerably larger than the uncertainty in the experimental density (which is about ±0.1 g/mL). We can be reasonably confident that the ring is not 24 carat gold, and in fact the measurements point toward the ring being composed of 22 carat gold.

To trust conclusions drawn from measurements, we must be sure the measurements are accurate and that they are of sufficient precision to be meaningful. This is a key consideration in designing experiments.

Summary

Properties of Materials. **Physical properties** are measured without changing the chemical composition of a sample. A physical change doesn't alter the chemical composition of the substances involved. **Solid, liquid,** and **gas** are the most common **states of matter.** The properties of the states of matter can be related to the different ways the individual atomic-size particles are organized. A **chemical property** describes a chemical reaction a substance undergoes. Formation or decomposition of a compound takes place by a chemical change that changes the chemical makeup of the substances involved. **Intensive properties** are independent of sample size; **extensive properties** depend on sample size.

Units of Measurement. **Qualitative observations** lack numerical information, whereas **quantitative observations** require numerical measurements. The units used for scientific measurements are based on the set of seven **SI base units**, which can be combined to give various **derived units**. These all can be scaled to larger or smaller sized units by applying **decimal multiplying factors**. In the laboratory we routinely measure length, volume, mass, and temperature. Convenient units for length and volume are, respectively, **centimeters** or **millimeters**, and **liters** or **milliliters**. **Mass** is a measure of the amount of matter in an object and differs from weight. Mass is measured with a **balance** and is expressed in units of **kilograms** or **grams**. Temperature is measured in units of **degrees Celsius** (or **Fahrenheit**) using a thermometer. For many calculations, temperature must be expressed in **kelvins (K)**. The zero point on the **Kelvin temperature scale** is called **absolute zero**.

Significant Figures. The **precision** of a measured quantity is expressed by the number of **significant figures** that it contains, which equals the number of digits known for sure plus the first one that possesses some uncertainty. Measured values are **precise** if they contain many significant figures and therefore differ from each other by small amounts. A measurement is **accurate** if its value lies very close to the true value. When measurements are combined in calculations, rules help us determine the correct number of significant figures in the answer (see below). **Exact numbers** are considered to have an infinite number of significant figures.

Dimensional Analysis. **Dimensional analysis (the factor-label method)** is based on the ability of units to undergo the same mathematical operations as numbers. **Conversion factors** are constructed from *valid relationships* between units. These relationships can be either equalities or **equivalencies** (indicated by the symbol ⇔) between units. Unit cancellation serves as a guide to the use of conversion factors and aids us in correctly setting up the arithmetic for a problem.

Density and Specific Gravity. **Density** is an intensive property equal to the ratio of a sample's mass to its volume. Besides serving as a means for identifying substances, density provides a conversion factor that relates mass to volume. **Specific gravity** is the ratio of the density of a substance to the density of water and is a **dimensionless** quantity. This serves as a convenient way to have density data available in a large number of mass and volume units.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Base SI units (Table 2.1, page 32)
The eight basic units of the SI system are used to derive the units for all scientific measurements.

SI prefixes (Table 2.4, page 35)

We use the prefixes to create larger and smaller units. They are also used as conversion factors for converting between differently sized units. Be sure you are familiar with the ones in bold type in Table 2.4.

Units in laboratory measurements (page 36)

Often we must convert among units commonly used for laboratory measurements.

Length: 1 m = 100 cm = 1000 mm

Volume: 1 L = 1000 mL = 1000 cm^3

Temperature conversions (pages 38 and 39)

Use these equations to convert between temperature scales.

$$t_F = \left(\frac{9\ °\text{F}}{5\ °\text{C}}\right)t_C + 32\ °\text{F} \qquad T_K = (t_C + 273.15)°\text{C}\left(\frac{1\ \text{K}}{1\ °\text{C}}\right)$$

Counting significant figures (page 42)

To gauge the quality of a measurement, we must know the number of significant figures it contains:

- All nonzero digits are significant.
- Zeros between significant digits, imbedded zeros, are significant.
- Zeros to the *left* of the first nonzero digit are never significant.
- Zeros on the end of a number (a) with a decimal point are significant; (b) those without a decimal point are assumed not to be significant. (To avoid confusion, scientific notation should be used.)

Significant figures: multiplication and division (page 44)

In these operations we round the answer to the same number of significant figures as the least precise factor (i.e. the factor with the fewest significant figures).

Significant figures: addition and subtraction (page 44)

We round the answer to match the same number of decimal places as the quantity with the fewest number of decimal places.

Significant figures: exact numbers (page 44)

Numbers such as those that arise from definitions do not affect the number of significant figures in the result of a calculation.

Density (page 51)

The density, d, relates mass, m, and volume, V, for a substance.

$$d = \frac{m}{V}$$

Density provides an equivalence between mass and volume, from which we can construct conversion factors to convert between mass and volume for a substance.

Specific gravity (page 54)

The specific gravity relates the density of a substance to the density of water,

$$\text{Specific gravity} = \frac{d_{\text{substance}}}{d_{\text{water}}}$$

Specific gravity is dimensionless, and when multiplied by the density of water, in the desired units, will give the density of the substance in those units.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Physical and Chemical Properties

2.1 Give five examples of physical properties.

2.2 How does a chemical property differ from a physical property?

2.3 Determine whether each of the following is a physical or chemical change, and explain your reasoning.

- **(a)** Copper conducts electricity.
- **(b)** Gallium metal will melt in your hand.
- **(c)** Bread turns brown in a toaster.
- **(d)** Wine turns to vinegar.
- **(e)** Cement hardens.

2.4 Determine whether each of the following is a physical or chemical change, and explain your reasoning.

- **(a)** Kernels of corn are heated to make popcorn.
- **(b)** Molten copper is mixed with molten gold to make an alloy.
- **(c)** Heavy cream is mixed vigorously to whipped cream.
- **(d)** Heavy cream is churned to make butter.
- **(e)** Aluminum soda cans are recycled.

Intensive and Extensive Properties

2.5 Distinguish between an extensive and an intensive property.

2.6 Determine whether each of the following is an intensive or extensive property, and justify your reasoning:

- **(a)** mass
- **(b)** boiling point
- **(c)** color
- **(d)** physical state

2.7 Determine whether each of the following is an intensive or extensive property, and justify your reasoning:

- **(a)** melting point
- **(b)** density
- **(c)** volume
- **(d)** surface area

States of Matter

2.8 Describe one or more physical properties of each state of matter that distinguishes it from the other states of matter:

- **(a)** gas
- **(b)** liquid
- **(c)** solid

2.9 At room temperature, what is the state of each of the following? If necessary, look up the information in a reference source.

- **(a)** hydrogen
- **(b)** aluminum
- **(c)** nitrogen
- **(d)** mercury

2.10 At room temperature, determine the appropriate phase for each of the following substances. (Look up the substance in data tables if needed.)

- **(a)** potassium chloride
- **(b)** carbon dioxide
- **(c)** ethyl alcohol
- **(d)** methane
- **(e)** sucrose

2.11 At room temperature, determine the appropriate phase for each of the following substances. (Look up the substance in data tables if needed.)

- **(a)** sodium chloride
- **(b)** ozone
- **(c)** Teflon
- **(d)** cholesterol
- **(e)** silicon dioxide

SI Units

2.12 Why must measurements always be written with a unit?

2.13 What is the only SI base unit that includes a prefix?

2.14 What is the meaning of each of the following prefixes?

- **(a)** centi
- **(b)** milli
- **(c)** kilo
- **(d)** micro
- **(e)** nano
- **(f)** pico
- **(g)** mega

2.15 What abbreviation is used for each of the prefixes named in Question 2.14?

2.16 What reference points do we use in calibrating the scale of a thermometer? What temperature on the Celsius scale do we assign to each of these reference points?

OH **2.17** In each pair, which is larger: **(a)** A Fahrenheit degree or a Celsius degree? **(b)** A Celsius degree or a kelvin? **(c)** A Fahrenheit degree or a kelvin?

Significant Figures; Dimensional Analysis

2.18 Define the term *significant figures.*

2.19 What is the difference between *accuracy* and *precision*?

2.20 Suppose a length had been reported to be 31.24 cm. What is the minimum uncertainty implied in this measurement?

2.21 Suppose someone suggested using the fraction 3 yd/1 ft as a conversion factor to change a length expressed in feet to its equivalent in yards. What is wrong with this conversion factor? Can we construct a valid conversion factor relating centimeters to meters from the equation 1 cm = 1000 m? Explain your answer.

2.22 In 1 hour there are 3600 seconds. By what conversion factor would you multiply 250 seconds to convert it to hours? By what conversion factor would you multiply 3.84 hours to convert it to seconds?

2.23 If you were to convert the measured length 4.165 ft to yards by multiplying by the conversion factor (1 yd/3 ft), how many significant figures should the answer contain? Why?

Density

2.24 Write the equation that defines density. Identify the symbols in the equation.

2.25 Silver has a density of 10.5 g cm^{-3}. Express this as an equivalence between mass and volume for silver. Write two conversion factors that can be formed from this equivalence for use in calculations.

Review Problems

SI Prefixes

2.26 What number should replace the question mark in each of the following?

(a) 1 cm = ? m
(b) 1 km = ? m
(c) 1 m = ? pm
(d) 1 dm = ? m
(e) 1 g = ? kg
(f) 1 cg = ? g

2.27 What numbers should replace the question marks below?

(a) 1 nm = ? m
(b) 1 µg = ? g
(c) 1 kg = ? g
(d) 1 Mg = ? g
(e) 1 mg = ? g
(f) 1 dg = ? g

Temperature Conversions

2.28 Perform the following conversions.

(a) 57 °C to °F
(b) 16 °C to °F
(c) 25.5 °F to °C
(d) 49 °F to °C
(e) 62 °C to K
(f) −31 °C to K

2.29 Perform the following conversions.

(a) 96 °F to °C
(b) −6 °F to °C
(c) −55 °C to °F
(d) 273 K to °C
(e) 299 K to °C
(f) 40.0 °C to K

2.30 A healthy dog has a temperature ranging from 37.2 °C to 39.2 °C. Is a dog with a temperature of 103.5 °F within the normal range?

2.31 The coldest permanently inhabited place on earth is the Siberian village of Oymyakon in Russia. In 1964 the temperature reached a shivering −96 °F! What is this temperature in °C?

2.32 Estimates of the temperature at the core of the sun range from 10 megakelvins to 25 megakelvins. What is this range in °C and °F?

2.33 Natural gas is mostly methane, a substance that boils at a temperature of 111 K. What is its boiling point in °C and °F?

2.34 Helium has the lowest boiling point of any liquid. It boils at 4 K. What is its boiling point in °C?

2.35 The atomic bomb detonated over Hiroshima, Japan, at the end of World War II raised the temperature on the ground below to about 6100 K. Is this hot enough to melt concrete? (Concrete melts at 2050 °C.)

Significant Figures

2.36 How many significant figures do the following measured quantities have?

(a) 37.53 cm
(b) 37.240 cm
(c) 202.0 g
(d) 0.00024 kg
(e) 0.07080 m
(f) 2400 mL

2.37 How many significant figures do the following measured quantities have?

(a) 0.0230 g
(b) 105.303 m
(c) 0.007 kg
(d) 614.00 mg
(e) 10 L
(f) 3.8105 mm

OH **2.38** Perform the following arithmetic and round off the answers to the correct number of significant figures. Include the correct units with the answers.

(a) 0.0023 m × 315 m
(b) 84.25 kg − 0.01075 kg
(c) (184.45 g − 94.45 g)/(31.4 mL − 9.9 mL)
(d) (23.4 g + 102.4 g + 0.003 g)/(6.478 mL)
(e) (313.44 cm − 209.1 cm) × 8.2234 cm

2.39 Perform the following arithmetic and round off the answers to the correct number of significant figures. Include the correct units with the answers.

(a) 3.58 g/1.739 mL
(b) 4.02 mL + 0.001 mL
(c) (22.4 g − 8.3 g)/(1.142 mL − 0.002 mL)
(d) (1.345 g + 0.022 g)/(13.36 mL − 8.4115 mL)
(e) (74.335 m − 74.332 m)/(4.75 s × 1.114 s)

Unit Conversions Using Dimensional Analysis

OH **2.40** Perform the following conversions.

(a) 32.0 dm/s to km/hr
(b) 8.2 mg/mL to µg/L
(c) 75.3 mg to kg
(d) 137.5 mL to L
(e) 0.025 L to mL
(f) 342 pm^2 to dm^2

2.41 Perform the following conversions.

(a) 92 dL to µm^3
(b) 22 ng to µg
(c) 83 pL to nL
(d) 230 km^3 to m^3
(e) 87.3 cm s^{-2} to km hr^{-2}
(f) 238 mm^2 to nm^2

2.42 Perform the following conversions. If necessary, refer to Tables 2.3 and 2.4.

(a) 36 in. to cm
(b) 5.0 lb to kg
(c) 3.0 qt to mL
(d) 1 cup (8 oz) to mL
(e) 55 mi/hr to km/hr
(f) 50.0 mi to km

2.43 Perform the following conversions. If necessary, refer to Tables 2.3 and 2.4.

(a) 250 mL to qt
(b) 3.0 ft to m
(c) 1.62 kg to lb
(d) 1.75 L to fluid oz
(e) 35 km/hr to mi/hr
(f) 80.0 km to mi

2.44 Perform the following conversions.

(a) 8.4 ft^2 to cm^2 **(b)** 223 mi^2 to km^2 **(c)** 231 ft^3 to cm^3

2.45 Perform the following conversions.

(a) 2.4 yd^2 to m^2 **(b)** 8.3 $in.^2$ to mm^2 **(c)** 9.1 ft^3 to L

2.46 The human stomach can expand to hold up to 4.2 quarts of food. A pistachio nut has a volume of about 0.9 mL. Use this information to estimate the maximum number of pistachios that can be eaten in one sitting.

2.47 In the movie *Cool Hand Luke* (1967), Luke wagers that he can eat 50 eggs in one hour. The prisoners and guards bet against him, saying, "Fifty eggs gotta weigh a good six pounds. A man's gut can't hold that." A peeled, chewed chicken egg has a volume of approximately 53 mL. If Luke's stomach has a volume of 4.2 quarts, does he have any chance of winning the bet?

ILW **2.48** The winds in a hurricane can reach almost 200 miles per hour. What is this speed in meters per second? (Assume three significant figures.)

2.49 A bullet is fired at a speed of 2435 ft/s. What is this speed expressed in kilometers per hour?

2.50 A bullet leaving the muzzle of a pistol was traveling at a speed of 2230 feet per second. What is this speed in miles per hour?

2.51 On average, water flows over Niagara Falls at a rate of 2.05×10^5 cubic feet per second. One cubic foot of water weighs 62.4 lb. Calculate the rate of water flow in tons of water per day. (1 ton = 2000 lb)

2.52 The brightest star in the night sky in the northern hemisphere is Sirius. Its distance from earth is estimated to be 8.7 light years. A light year is the distance light travels in one year. Light travels at a speed of 3.00×10^8 m/s. Calculate the distance from earth to Sirius in miles. (1 mi = 5280 ft).

2.53 One degree of latitude on the earth's surface equals 60.0 nautical miles. One nautical mile equals 1.151 statute miles. (A *statute mile* is the distance over land that we normally associate with the unit mile). Calculate the circumference of the earth in statute miles.

2.54 The deepest point in the earth's oceans is found in the Mariana Trench, a deep crevasse located about 1000 miles southeast of Japan beneath the Pacific Ocean. Its maximum depth is 6033.5 fathoms. One fathom is defined as 6 feet. Calculate the depth of the Mariana Trench in meters.

2.55 At sea level, our atmosphere exerts a pressure of about 14.7 lb/in^2, which means that each square inch of your body experiences a force of 14.7 lb from the air that surrounds you. As you descend below the surface of the ocean, the pressure produced by the seawater increases by about 14.7 lb/in^2 for every 10 meters of depth. In the preceding problem you calculated the maximum depth of the Mariana Trench, located in the Pacific Ocean. What is the approximate pressure in pounds per square inch and in tons per square inch exerted by the sea at the deepest point of the trench? (1 ton = 2000 lb)

Density and Specific Gravity

2.56 A sample of kerosene weighs 36.4 g. Its volume was measured to be 45.6 mL. What is the density of the kerosene in g mL^{-1}?

2.57 A block of magnesium has a mass of 14.3 g and a volume of 8.46 cm^3. What is the density of magnesium in g/cm^3?

OH **2.58** Acetone, the solvent in some nail polish removers, has a density of 0.791 g/mL. What is the volume, in mL, of 25.0 g of acetone?

2.59 A glass apparatus contains 26.223 g of water when filled at 25 °C. At this temperature, water has a density of 0.99704 g/mL. What is the volume, in mL, of the apparatus?

2.60 Chloroform, a chemical once used as an anesthetic, has a density of 1.492 g/mL. What is the mass in grams of 185 mL of chloroform?

2.61 Gasoline has a density of about 0.65 g/mL. How much does 34 L (approximately 18 gallons) weigh in kilograms? In pounds?

ILW **2.62** A graduated cylinder was filled with water to the 15.0 mL mark and weighed on a balance. Its mass was 27.35 g. An object made of silver was placed in the cylinder and completely submerged in the water. The water level rose to 18.3 mL. When reweighed, the cylinder, water, and silver object had a total mass of 62.00 g. Calculate the density of silver in g cm^{-3}.

2.63 Titanium is a metal used to make golf clubs. A rectangular bar of this metal measuring 1.84 cm × 2.24 cm × 2.44 cm was found to have a mass of 45.7 g. What is the density of titanium in g mL^{-1}?

2.64 The space shuttle uses liquid hydrogen as its fuel. The external fuel tank used during takeoff carries 227,641 lb of hydrogen with a volume of 385,265 gallons. Calculate the density of liquid hydrogen in units of lb/gal and g/mL. (Express your answer to three significant figures.) What is the specific gravity of liquid hydrogen?

2.65 You are planning to make a cement driveway that has to be 10.1 feet wide, 32.3 feet long, and 4.00 inches deep on average. The specific gravity of concrete is 0.686. How many kilograms of concrete are needed for the job?

Additional Exercises

2.66 Some time ago, a U.S. citizen traveling in Canada observed that the price of regular gasoline was 0.959 Canadian dollars per liter. The exchange rate at the time was 1.142 Canadian dollars per one U.S. dollar. Calculate the price of the Canadian gasoline in units of U.S. dollars per gallon. (Just the week before, the traveler had paid $2.249 per gallon in the United States.)

OH **2.67** You are the science reporter for a daily newspaper, and your editor has asked you to write a story based on a report in the scientific literature. The report states that analysis of the sediments in Hausberg Tarn (elevation 4350 m) on the side of Mount Kenya (elevation 4600–4700 m) shows that the average temperature of the water rose by 40 °C between 350 BC and 450 AD. Your editor wants all the data expressed in the English system of units. Make the appropriate conversions.

2.68 An astronomy Web site states that neutron stars have a density of 1.00×10^8 tons per cubic centimeter. The site does not specify whether "tons" means metric tons (1 metric ton = 1000 kg) or English tons (1 English ton = 2000 pounds). How many grams would one teaspoon of a neutron star weigh, if the density were in metric tons per cm^3? How many grams would the teaspoon weigh if the density were in English tons per cm^3? (One teaspoon is approximately 4.93 mL.)

2.69 The star Arcturus is 3.50×10^{14} km from the earth. How many days does it take for light to travel from Arcturus to earth? What is the distance to Arcturus in light years? One light year is the distance light travels in one year (365 days); light travels at a speed of 3.00×10^8 m/s.

***2.70** A pycnometer is a glass apparatus used for accurately determining the density of a liquid. When dry and empty, a certain pycnometer had a mass of 27.314 g. When filled with distilled water at 25.0 °C, it weighed 36.842 g. When filled with chloroform (a liquid once used as an anesthetic before its toxic properties were known), the apparatus weighed 41.428 g. At 25.0 °C, the density of water is 0.99704 g/mL. **(a)** What is the volume of the pycnometer? **(b)** What is the density of chloroform?

2.71 Radio waves travel at the speed of light, 3.00×10^8 m/s. If you were to broadcast a question to an astronaut on the moon, which is 239,000 miles from earth, what is the minimum time that you would have to wait to receive a reply?

2.72 Suppose you have a job in which you earn $4.50 for each 30 minutes that you work.

(a) Express this information in the form of an equivalence between dollars earned and minutes worked.

(b) Use the equivalence defined in (a) to calculate the number of dollars earned in 1 hr 45 min.

(c) Use the equivalence defined in (a) to calculate the number of minutes you would have to work to earn $17.35.

2.73 When an object floats in water, it displaces a volume of water that has a weight equal to the weight of the object. If a ship has a weight of 4255 tons, how many cubic feet of seawater will it displace? Seawater has a density of 1.025 g cm^{-3}; 1 ton = 2000 lb.

2.74 Aerogel or "solid smoke" is a novel material that is made of silicon dioxide, like glass, but is a thousand times less dense than glass because it is extremely porous. Material scientists at NASA's Jet Propulsion Laboratory created the lightest aerogel ever in 2002, with a density of 0.00011 pounds per cubic inch. The material was used for thermal insulation in the 2003 Mars Exploration Rover. If the maximum space for insulation in the spacecraft's hull was 2510 cm^3, what mass (in grams) did the aerogel insulation add to the spacecraft?

Aerogel *(NASA/JPL)*

2.75 A liquid known to be either ethanol (ethyl alcohol) or methanol (methyl alcohol) was found to have a density of 0.798 ± 0.001 g/mL. Consult tabulated data to determine which liquid it is. What other measurements could help to confirm the identity of the liquid?

2.76 An unknown liquid was found to have a density of 69.22 lb/ft^3. The density of ethylene glycol (the liquid used in antifreeze) is 1.1088 g/mL. Could the unknown liquid be ethylene glycol?

2.77 When an object is heated to a high temperature, it glows and gives off light. The color balance of this light depends on the temperature of the glowing object. Photographic lighting is described, in terms of its color balance, as a temperature in kelvins. For example, a certain electronic flash gives a color balance (called color temperature) rated at 5800 K. What is this temperature expressed in °C?

OH **2.78** There exists a single temperature at which the value reported in °F is numerically the same as the value reported in °C. What is this temperature?

***2.79** In the text, the Kelvin scale of temperature is defined as an absolute scale in which one Kelvin degree unit is the same size as one Celsius degree unit. A second absolute temperature scale exists called the Rankine scale. On this scale, one Rankine degree unit (°R) is the same size as one Fahrenheit degree unit. **(a)** What is the only temperature at which the Kelvin and Rankine scales possess the same numerical value? Explain your answer. **(b)** What is the boiling point of water expressed in °R?

***2.80** Density measurements can be used to analyze mixtures. For example, the density of solid sand (without air spaces) is about 2.84 g/mL. The density of gold is 19.3 g/mL. If a 1.00 kg sample of sand containing some gold has a density of 3.10 g/mL (without air spaces), what is the percentage of gold in the sample?

***2.81** An artist's statue has a surface area of 14.6 ft^2. The artist plans to apply gold leaf to the statue and wants the coating to be 2.50 μm thick. If the price of gold were $1,125.10 per troy ounce, how much would it cost to give the statue its gold coating? (1 troy ounce = 31.1035 g; the density of gold is 19.3 g/mL.)

***2.82** A cylindrical metal bar has a diameter of 0.753 cm and a length of 2.33 cm. It has a mass of 8.423 g. Calculate the density of the metal in the units lb/ft^3.

2.83 What is the volume in cubic millimeters of a 3.54 carat diamond, given that the density of diamond is 3.51 g/mL? (1 carat = 200 mg)

***2.84** Because of the serious consequences of lead poisoning, the Federal Centers for Disease Control in Atlanta has set a threshold of concern for lead levels in children's blood. This threshold was based on a study that suggested that lead levels in blood as low as *10 micrograms of lead per deciliter of blood* can result in subtle effects of lead toxicity. Suppose a child had a lead level in her blood of 2.5×10^{-4} grams of lead per liter of blood. Is this person in danger of exhibiting the effects of lead poisoning?

***2.85** Gold has a density of 19.31 g cm^{-3}. How many grams of gold are required to provide a gold coating 0.500 mm thick on a ball bearing having a diameter of 2.000 mm?

***2.86** A Boeing 747 jet airliner carrying 568 people burns about 5.0 gallons of jet fuel per mile. What is the rate of fuel consumption in units of gallons per person per mile? Is this better or worse than the rate of fuel consumption in an automobile carrying two people that gets 21.5 miles per gallon? If the airliner were making the 3470 mile trip from New York to London, how many pounds of jet fuel would be consumed? (Jet fuel has a density of 0.803 g/mL.)

Exercises in Critical Thinking

2.87 Find two or more Web sites that give the values for each of the seven base SI units. Keeping in mind that not all Web sites provide reliable information, which Web site do you believe provides the most reliable values? Justify your answer.

2.88 Reference books such as the *Handbook of Chemistry and Physics* report the specific gravities of substances instead of their densities. Find the definition of specific gravity, and discuss the relative merits of specific gravity and density in terms of their usefulness as a physical property.

***2.89** A student used a 250 mL graduated cylinder having volume markings every 2 mL to carefully measure 100 mL of water for an experiment. A fellow student said that by reporting the volume as "100 mL" in her lab notebook, she was only entitled to one significant figure. The first student disagreed. Why did her fellow student say the reported volume had only one significant figure? Considering the circumstances, how many significant figures are in her measured volume? Justify your answer.

***2.90** Download a table of data for the density of water between its freezing and boiling points. Use a spreadsheet program to plot (a) the density of water versus temperature and (b) the volume of a kilogram of water versus temperature. Interpret the significance of these plots.

2.91 List the physical and chemical properties mentioned in this chapter. What additional physical and chemical properties can you think of to extend this list?

***2.92** A barge pulled by a tugboat can be described as a rectangular box that is open on the top. A certain barge is 30.2 feet wide and 12.50 feet high, with the base of each side being 116 feet long. If the barge itself weighs 6.58×10^4 pounds, what will be the draft (depth in the water) if the cargo weighs 1.12×10^6 pounds in (a) seawater with a density of 1.025 g/mL and (b) freshwater with a density of 0.997 g/mL?

3

Elements, Compounds, and the Periodic Table

Chapter Outline

3.1 | Internal Structure of the Atom

3.2 | The Periodic Table

3.3 | Metals, Nonmetals, and Metalloids

3.4 | Ionic Compounds

3.5 | Nomenclature of Ionic Compounds

3.6 | Molecular Compounds

3.7 | Nomenclature of Molecular Compounds

A supernova, such as the one whose remnants are shown in the photograph taken by the Hubble space telescope, occurs when a large star collapses and explodes. It is in such explosions that particles of matter with names such as electrons, protons, and neutrons are forced together to form atoms of the elements that make up our universe. As you will learn in this chapter, these atomic particles are important in understanding the make-up of elements and the kinds of compounds elements form when they undergo chemical reactions. NASA, ESA, and M. Livio and the Hubble 20th Anniversary Team (STScI)

This Chapter in Context

Students sometimes say that "chemistry is a foreign language." This statement is not far from the truth. We can consider the elements in the periodic table to be our new alphabet; the formulas for compounds are the words of chemistry; and the balanced equations that show how those compounds react with each other are the sentences of this new language. Learning the language of chemistry will help you succeed because you will be able to concentrate on new concepts that depend on your being fluent in your new language.

In Chapter 1 we introduced the broad scope and nature of the subject of chemistry, elements, classification of matter, the atomic theory, formulas, and reactions. In Chapter 2, we discussed the ways that precise and accurate measurements and calculations are central to all sciences, especially chemistry. Now we turn our attention to atoms, the periodic table, chemical compounds, and naming these compounds. We will take a closer look at the particles that make up the atoms, and how these particles define the identity of the elements. Then, we will use this information to arrange the elements into a table that is a storehouse of relationships, trends, and similarities among the elements. These elements combine to form compounds, and the type of compound formed can be determined by the makeup of the atoms. Finally, we will introduce you to *chemical nomenclature*—the system used to name chemical compounds.

3.1 | Internal Structure of the Atom

The earliest theories about atoms imagined them to be indestructible and totally unable to be broken into smaller pieces. However, as you probably know, atoms are not quite as indestructible as Dalton and other early philosophers had thought. During the late 1800s and early 1900s, experiments were performed that demonstrated that atoms are composed of **subatomic particles**. From this work the current theoretical model of atomic structure evolved. We will examine it in general terms in this chapter. A more detailed discussion of the electronic structure of the atom will follow in Chapter 8.

Discovery of the Electron, Proton, and Neutron

Our current knowledge of atomic structure was pieced together from facts obtained from experiments by scientists that began in the nineteenth century. In 1834, Michael Faraday discovered that the passage of electricity through aqueous solutions could cause chemical changes. This was the first hint that matter was electrical in nature. Later in that century, scientists began to experiment with *gas discharge tubes* in which a high-voltage electric current was passed through a gas at low pressure in a glass tube (Figure 3.1). Such a tube is fitted with a pair of metal *electrodes*, and when the electricity begins to flow between them, the gas in the tube glows. This flow of electricity is called an *electric discharge*, which is how the tubes got their name.

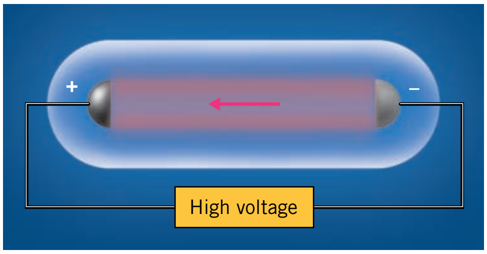


Figure 3.1 | **A gas discharge tube.** Cathode rays flow from the negatively charged cathode to the positively charged anode.

The physicists who first studied this phenomenon did not know what caused the tube to glow, but tests soon revealed that negatively charged particles were moving from the negative electrode (the **cathode**) to the positive electrode (the **anode**). The physicists called these emissions *rays,* and because the rays came from the cathode, they were called **cathode rays.**

In 1897, the British physicist J. J. Thomson modified a *cathode ray tube,* a special gas discharge tube, to make quantitative measurements of the properties of cathode rays, Figure 3.2. In Thomson's tube, a beam of cathode rays was focused on a glass surface coated with a phosphor, a substance that glows when the cathode rays strike it (point 1). The cathode ray beam passed between the poles of a magnet and between a pair of metal electrodes that could be given electrical charges. The magnetic field tends to bend the beam in one direction (toward point 2), while the charged electrodes bend the beam in the opposite direction (toward point 3). By adjusting the charge on the electrodes, the two effects can be made to cancel, and from the amount of charge on the electrodes required to balance the effect of the magnetic field, Thomson was able to calculate the first bit of quantitative information about a cathode ray particle—the ratio of its charge to its mass (often expressed as *e/m,* where *e* stands for charge and *m* stands for mass). The charge-to-mass ratio has a value of -1.76×10^8 coulombs/gram, where the coulomb (C) is a standard unit of electrical charge and the negative sign reflects the negative charge on the particle.

Many experiments were performed using the cathode ray tube, and they demonstrated that cathode ray particles are in all matter. They are, in fact, *electrons.*

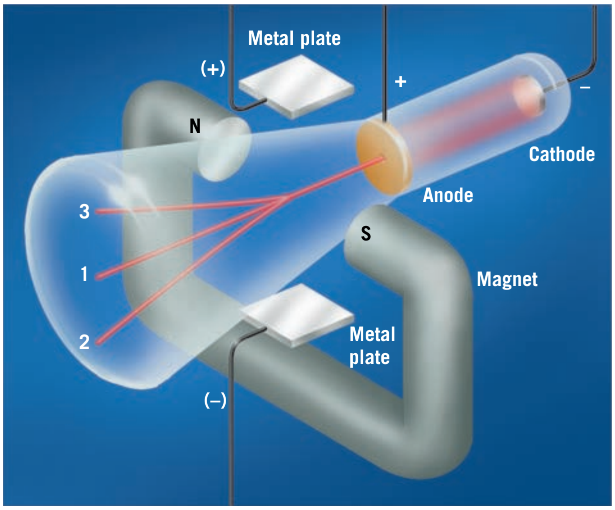


Figure 3.2 | **Thomson's cathode ray tube,** which was used to measure the charge-to-mass ratio for the electron.

Measuring the Charge and Mass of the Electron

In 1909, a researcher at the University of Chicago, Robert Millikan, designed an experiment that enabled him to measure the electron's charge (Figure 3.3). During the experiment he sprayed a fine mist of oil droplets above a pair of parallel metal plates, the top one of which had a small hole in it. As the oil drops settled, some would pass through this hole into the space between the plates, where he would irradiate them briefly with X rays. The X rays knocked electrons off molecules in the air, and the electrons became attached to the oil drops, which thereby were given an electrical charge. By observing the rate of fall of the charged drops both when the metal plates were electrically charged and when they were not, Millikan was able to calculate the amount of charge carried by each drop. When he examined his results, he found that all the values he obtained were whole-number multiples of -1.60×10^{-19} C. He reasoned that since a drop could only pick up whole numbers of electrons, this value must be the charge carried by each individual electron.

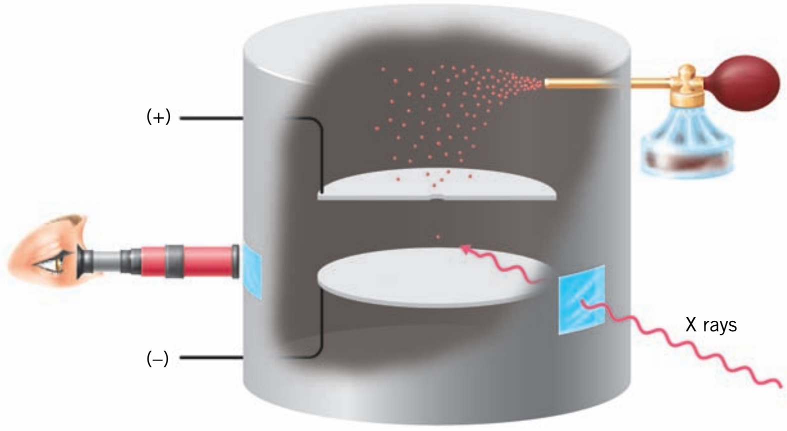


Figure 3.3 | **Millikan's oil drop experiment.** Electrons, which are ejected from molecules in the air by the X rays, are picked up by very small drops of oil falling through the tiny hole in the upper metal plate. By observing the rate of fall of the charged oil drops, with and without electrical charges on the metal plates, Millikan was able to calculate the charge carried by an electron.

Once Millikan had measured the electron's charge, its mass could then be calculated from Thomson's charge-to-mass ratio. This mass was calculated to be 9.09×10^{-28} g. More precise measurements have since been made, and the mass of the electron is currently reported to be $9.1093897 \times 10^{-28}$ g. Thomson's early measurements are in good agreement with today's more precise measurements.

Discovery of the Proton

The removal of electrons from an atom gives a positively charged particle (called an *ion*). To study these particles, a modification was made in the construction of the cathode ray tube to produce a new device called a *mass spectrometer*. This apparatus is described in *On the Cutting Edge 3.1* and was used to measure the charge-to-mass ratios of positive ions. These ratios were found to vary, depending on the chemical nature of the gas in the discharge tube, showing that their masses also varied. The lightest positive particle observed was produced when hydrogen was in the tube, and its mass was about 1800 times as heavy as an electron. When other gases

ON THE CUTTING EDGE **3.1**

The Mass Spectrometer and the Experimental Measurement of Atomic Masses

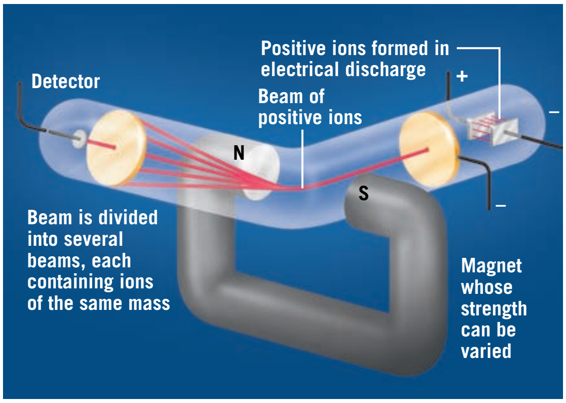
When a spark is passed through a gas, electrons are knocked off the gas molecules. Because electrons are negatively charged, the particles left behind carry positive charges; they are called *positive ions.* These positive ions have different masses, depending on the masses of the molecules from which they are formed. Thus, some molecules have large masses and give heavy ions, while others have small masses and give light ions.

The device that is used to study the positive ions produced from gas molecules is called a *mass spectrometer* (illustrated in the figure at the right). In a mass spectrometer, positive ions are created by passing an electrical spark (called an *electric discharge*) through a sample of the particular gas being studied. As the positive ions are formed, they are attracted to a negatively charged metal plate that has a small hole in its center. Some of the positive ions pass through this hole and travel onward through a tube that passes between the poles of a powerful magnet.

One of the properties of charged particles, both positive and negative, is that their paths become curved as they pass through a magnetic field. This is exactly what happens to the positive ions in the mass spectrometer as they pass between the poles of the magnet. However, the extent to which their paths are bent depends on the masses of the ions. This is because the path of a heavy ion, like that of a speeding cement truck, is difficult to change, but the path of a light ion, like that of a motorcycle, is influenced more easily. As a result, heavy ions emerge from between the magnet's poles along different lines than the lighter ions. In effect, an entering beam containing ions of different masses is sorted by the magnet into a number of beams, each containing ions of the same mass. This spreading out of the ion beam thus produces an array of different beams called a *mass spectrum*. There are many types of mass spectrometers. Here the array of beams can be detected by exposing photographic film.

In another type of mass spectrometer, the strength of the magnetic field is gradually changed, which sweeps the beams of ions across a detector located at the end of the tube. As a beam of ions strikes the detector, its intensity is measured and the masses of the particles in the beam are computed based on the strength of the magnetic field, the speed of the particles, and the geometry of the apparatus.

Among the benefits derived from measurements using the mass spectrometer are very accurate isotopic masses and relative isotopic abundances. These serve as the basis for the very precise values of the atomic masses that you find in the periodic table. (Isotopes are atoms of the same element with slightly different masses. They are discussed on page 68.)


Positive ions formed in electrical discharge
+
Detector
Beam of positive ions
−
N
S
−
Beam is divided into several beams, each containing ions of the same mass
Magnet whose strength can be varied

were used, their masses always seemed to be whole-number multiples of the mass observed for hydrogen ions. This suggested the possibility that clusters of the positively charged particles made from hydrogen atoms made up the positively charged particles of other gases. The hydrogen atom, minus an electron, thus seemed to be a fundamental particle in all matter and was named the *proton*, after the Greek word *proteios,* meaning "of first importance."

Discovery of the Atomic Nucleus

Early in the twentieth century, Hans Geiger and Ernest Marsden, working under Ernest Rutherford at Great Britain's Manchester University, studied what happened when *alpha rays* hit thin gold foils. Alpha rays are composed of particles having masses four times those of the proton and bearing two positive charges; they are emitted by certain unstable atoms in a phenomenon called *radioactive decay*. Most of the alpha particles sailed right on through as if the foils were virtually empty space (Figure 3.4). A significant number of alpha particles, however, were deflected at very large angles. Some were even deflected backward, as if they had hit a stone wall. Rutherford was so astounded that he compared the effect to that of firing a 15 inch artillery shell at a piece of tissue paper and having it come back and hit the gunner! From studying the angles of deflection of the particles, Rutherford reasoned that only something extraordinarily massive and positively charged

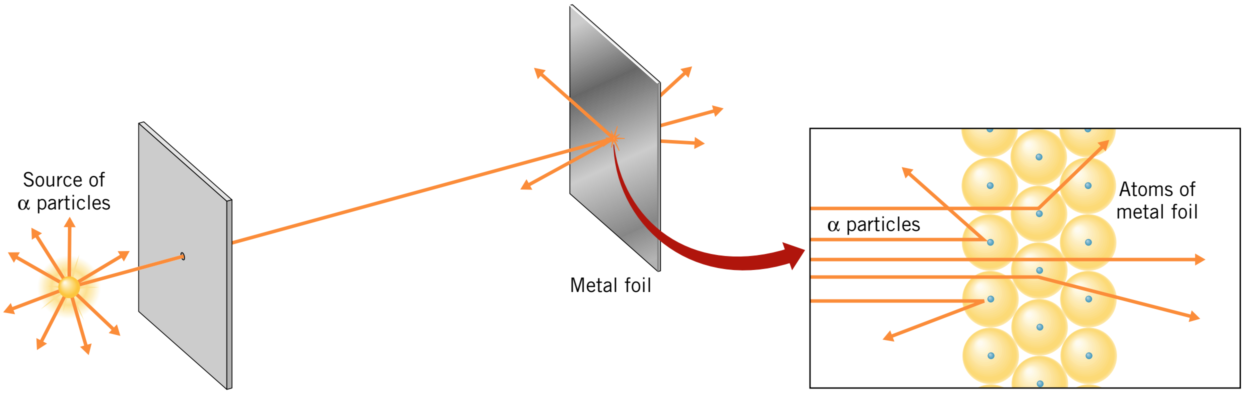


Figure 3.4 | **Some alpha particles are deflected by a thin gold foil.** Some hit something very massive head-on and are deflected backward. Many sail through. Some, making near misses with the massive "cores" (nuclei), are still deflected, because alpha particles have the same kind of charge (+) as these cores.

could cause such an occurrence. Since most of the alpha particles went straight through, he further reasoned that the metal atoms in the foils must be mostly empty space. Rutherford's ultimate conclusion was that virtually all of the mass of an atom must be concentrated in a particle having a very small volume located in the center of the atom. He called this massive particle the atom's *nucleus*.

Discovery of the Neutron

From the way alpha particles were scattered by a metal foil, Rutherford and his students were able to estimate the number of positive charges on the nucleus of an atom of the metal. This had to be equal to the number of protons in the nucleus. When they computed the nuclear mass based on this number of protons, however, the value always fell short of the actual mass. In fact, Rutherford found that only about half of the nuclear mass could be accounted for by protons. This led him to suggest that there were other particles in the nucleus that had a mass close to or equal to that of a proton, but with no electrical charge. This suggestion initiated a search that finally ended in 1932 with the discovery of the *neutron* by Sir James Chadwick, a British physicist.

■ For his work, Sir Chadwick earned the Nobel Prize in physics in 1935.

Subatomic Particles

The experiments described above showed that atoms are composed of three principal kinds of subatomic particles: **protons**, **neutrons**, and **electrons**. Experiments also revealed that at the center of an atom there exists a very tiny, extremely dense core called the *nucleus*, which is where an atom's protons and neutrons are found. Because they are found in nuclei, protons and neutrons are sometimes called **nucleons**. The electrons in an atom surround the nucleus and fill the remaining volume of the atom. (*How* the electrons are distributed around the nucleus is the subject of Chapter 8.) The properties of the subatomic particles are summarized in Table 3.1, and the general structure of the atom is illustrated in Figure 3.5.

■ Physicists have discovered a large number of subatomic particles, but protons, neutrons, and electrons are the only ones that will concern us at this time.

■ Protons are in all nuclei. Except for ordinary hydrogen, all nuclei also contain neutrons.

Table 3.1 **Properties of Subatomic Particles**

Particle	Mass (g)	Electrical Charge	Symbol
Electron	$9.1093897 \times 10^{-28}$	1−	${}^{0}_{-1}e$
Proton	$1.6726231 \times 10^{-24}$	1+	${}^{1}_{1}\mathrm{H}^{+}$, ${}^{1}_{1}p$
Neutron	$1.6749286 \times 10^{-24}$	0	${}^{1}_{0}n$

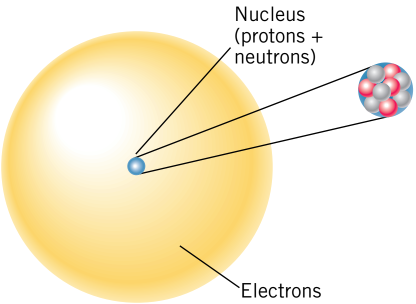


Figure 3.5 | **The internal structure of a atom.** An atom is composed of a tiny nucleus that holds all of the protons (red) and neutrons (grey). The electrons are in the space outside the nucleus.

■ The binding energy of nucleons is discussed in Chapter 21. This binding energy is what allowed for the easy formation of the elements up to iron.

As noted above, two of the subatomic particles carry electrical charges. Protons carry a single unit of **positive charge,** and electrons carry a single unit of **negative charge.** Two particles that have the same electrical charge repel each other, and two particles that have opposite charges attract each other. In an atom the negatively charged electrons are attracted to the positively charged protons. In fact, it is this attraction that holds the electrons around the nucleus. Neutrons have no charge and are electrically neutral.

Because of their identical charges, electrons repel each other. The repulsions between the electrons keep them spread out throughout the volume of the atom, and it is the *balance* between the attractions the electrons feel toward the nucleus and the repulsions they feel toward each other that controls the sizes of atoms.

Protons also repel each other, but they are able to stay together in the small volume of the nucleus because their repulsions are apparently offset by powerful nuclear binding forces that involve other subatomic particles that are studied in particle physics.

Matter as we generally find it in nature appears to be electrically neutral, which means that it contains equal numbers of positive and negative charges. Therefore, *in a neutral atom, the number of electrons must equal the number of protons.*

The proton and neutron are much more massive than the electron, about 1800 times heavier, so in any atom almost all of the atomic mass is contributed by the particles found in the nucleus. It is also interesting to note, however, that the diameter of the atom is approximately 10,000 times the diameter of its nucleus, so almost all of the *volume* of an atom is occupied by its electrons, which fill the space around the nucleus. (To place this on a more meaningful scale, if the nucleus was 1 ft in diameter, it would lie at the center of an atom with a diameter of approximately 1.9 miles or 10,000 feet!)

Atomic Numbers and Mass Numbers

TOOLS

Number of subatomic particles in atoms

What distinguishes one element from another is the number of protons in the nuclei of its atoms, because *all of the atoms of a particular element have an identical number of protons.* In fact, this allows us to redefine an **element** as *a substance whose atoms all contain the identical number of protons.* Thus, each element has associated with it a unique number, which we call its **atomic number** *(Z)*, that equals the number of protons in the nucleus of each of its atoms.

$$\text{Atomic number } (Z) = \text{number of protons}$$

Most elements exist in nature as mixtures of similar atoms called *isotopes* that differ only in mass. What makes isotopes of the same element different are the numbers of neutrons in their nuclei. *The* **isotopes** *of a given element have atoms with the same number of protons but different numbers of neutrons.* The numerical sum of the protons and neutrons in the atoms of a particular isotope is called the **mass number** *(A)* of the isotope.

$$\text{Isotope mass number } (A) = (\text{number of protons}) + (\text{number of neutrons})$$

Therefore, every isotope is fully defined by two numbers, its atomic number and its mass number. Sometimes these numbers are added to the left of the chemical symbol as a subscript and a superscript, respectively. Thus, if X stands for the chemical symbol for the element, an isotope of X is represented as

TOOLS

Atomic symbols for isotopes

$${}^{A}_{Z}X$$

The isotope of uranium used in nuclear reactors, for example, can be symbolized as follows:

$$\begin{array}{r l} \text{Mass number (number of protons and number of neutrons)} \searrow & \\ & {}^{235}_{92}\text{U} \\ \text{Atomic number (number of protons)} \nearrow & \\ & \text{Uranium-235} \end{array}$$

As indicated, the name of this isotope is uranium-235 or U-235. Each neutral atom contains 92 protons and $(235 - 92) = 143$ neutrons as well as 92 electrons. In writing the symbol for the isotope, the atomic number is often omitted because it is redundant. Every atom of uranium has 92 protons, and every atom that has 92 protons is an atom of uranium. Therefore, this uranium isotope can be represented simply as ^{235}U.

■ For a neutral atom, the atomic number equals both the number of protons and the number of electrons.

In naturally occurring uranium, a more abundant isotope is ^{238}U. Atoms of this isotope also have 92 protons, but the number of neutrons is 146. Thus, atoms of ^{235}U and ^{238}U have the identical number of protons but differ in the numbers of neutrons.

Example 3.1
Counting Protons, Neutrons, and Electrons

How many electrons, protons, and neutrons does the isotope Cr-52 have?

■ **Analysis:** This problem asks for all three of the major subatomic particles in the Cr-52 isotope that has a mass of 52.

■ **Assembling the Tools:** First, we have to determine the identity of the element from the symbol using the table inside the front cover. All three of the tools for subatomic particles must be used:

$$\text{Number of protons} = \text{atomic number} = Z$$
$$\text{Number of electrons} = \text{atomic number} = Z$$
$$\text{Number of neutrons} = \text{mass number} - \text{atomic number} = A - Z$$

■ **Solution:** We find that Cr is the symbol for chromium, so $Z = 24$ and $A = 52$, and we conclude

$$\text{Protons} = 24; \qquad \text{Electrons} = 24; \qquad \text{Neutrons} = 52 - 24 = 28$$

■ **Is the Answer Reasonable?** One check is to be sure that the sum of the number of protons and neutrons is the isotope mass number. A second check is that the number of any of the particles is not larger than the isotope mass number (the largest number given in the problem), and in most cases the number of electrons, protons, or neutrons is usually close to half of the mass number. A final check is that the number of protons equals the number of electrons because it is a neutral atom. Our answers fulfill these conditions.

Practice Exercises

3.1 | Write the symbol for the isotope of plutonium (Pu) that contains 146 neutrons. How many electrons does it have? (*Hint:* Review the tools for writing isotope symbols and counting electrons.)

3.2 | How many protons, neutrons, and electrons are in each atom of $^{35}_{17}Cl$?

3.3 | In Practice Exercise 3.2, can we discard the 35 or the 17 or both from the symbol without losing the ability to solve the problem? Explain your reasoning.

Relative Atomic Masses of Elements

Before subatomic particles were discovered, a significant body of data had already been developed that showed that atoms of different elements had different distinctive masses. In fact, one of the most useful concepts to come from Dalton's atomic theory is that atoms of an element have a constant, characteristic **atomic mass** (or **atomic weight**). This concept opened the door to the determination of chemical formulas and ultimately to one of the most useful devices chemists have for organizing chemical information, the *periodic table of the elements*. But how could the masses of atoms be measured without a knowledge of atomic structure?

Individual atoms are much too small to weigh in the traditional manner. However, the *relative masses* of the atoms of elements can be determined *provided we know the ratio in which the atoms occur in a compound.* Let's look at an example to see how this could work.

Hydrogen (H) combines with the element fluorine (F) to form the compound hydrogen fluoride. Each molecule of this compound contains one atom of hydrogen and one atom of fluorine, which means that in *any* sample of this substance the fluorine-to-hydrogen *atom ratio* is always 1 to 1. It is also found that when a sample of hydrogen fluoride is decomposed, the mass of fluorine obtained is always 19.0 times larger than the mass of hydrogen, so the fluorine-to-hydrogen *mass ratio* is always 19.0 to 1.00.

F-to-H atom ratio: 1 to 1
F-to-H mass ratio: 19.0 to 1.00

TOOLS
Relative atomic masses

How could a 1-to-1 atom ratio give a 19.0-to-1.00 mass ratio? *It could do this only if each fluorine atom is 19.0 times heavier than each H atom.*

Notice that even though we haven't found the actual masses of F and H atoms, we now know how their masses compare (i.e., we know their *relative masses*). Similar procedures, with other elements in other compounds, are able to establish relative mass relationships among the other elements as well. What we need next is a way to place all of these masses on the same mass scale.

Carbon-12: Standard for the Atomic Mass Scale

To establish a uniform mass scale for atoms it is necessary to select a standard against which the relative masses can be compared. Currently, the agreed-upon reference uses the most abundant isotope of carbon, carbon-12, ^{12}C. From this reference, one atom of this isotope is *exactly* 12 units of mass, which are called **atomic mass units.** Some prefer to use the symbol **amu** for the atomic mass unit. The internationally accepted symbol is **u,** which is the symbol we will use throughout the rest of the book. By assigning 12 u to the mass of one atom of ^{12}C, the size of the atomic mass unit is established to be $\frac{1}{12}$ of the mass of a single carbon-12 atom:

■ In biology, the atomic-mass unit is sometimes called a dalton. 1 u = 1 dalton.

1 atom of ^{12}C has a mass of 12 u (exactly)
1 u equals $\frac{1}{12}$ the mass of 1 atom of ^{12}C (exactly)

In modern terms, the atomic mass of an element is the average mass of the element's atoms (as they occur in nature) relative to an atom of carbon-12, which is assigned a mass of 12 units. Thus, if an average atom of an element has a mass twice that of a ^{12}C atom, its atomic mass would be 24 u.

The definition of the size of the atomic mass unit is really quite arbitrary. It could just as easily have been selected to be $\frac{1}{24}$ of the mass of a carbon atom, or $\frac{1}{10}$ of the mass of an iron atom, or any other value. Why $\frac{1}{12}$ of the mass of a ^{12}C atom? First, carbon is a very common element, available to any scientist. Second, and most important, by choosing the atomic mass unit of this size, the atomic masses of nearly all of the other elements are almost whole numbers, with the lightest atom (hydrogen) having a mass of approximately 1 u.

■ Even the smallest laboratory sample of an element has so many atoms that the relative proportions of the isotopes is constant.

■ Tritium, ^{3}H, is a third isotope of hydrogen, but the naturally occurring amount is so small that we need not consider it.

Chemists generally work with whatever *mixture* of isotopes that occur naturally for a given element. Because the composition of this isotopic mixture is very nearly constant regardless of the source of the element, we can speak of an *average mass of an atom* of the element—average in terms of mass. For example, naturally occurring hydrogen is almost entirely a mixture of two isotopes in the relative proportions given in Table 3.2 on page 71. The "average mass of an atom" of the element hydrogen, as it occurs in nature, has a mass that is 0.083992 times that of a ^{12}C atom. Since $0.083992 \times 12.000\ u = 1.0079\ u$, the average atomic mass of hydrogen is 1.0079 u. Notice that this average value is only a little larger than the atomic mass of ^{1}H because naturally occurring hydrogen contains mostly ^{1}H and only a little ^{2}H, as shown in Table 3.2.

In general, the mass number of an isotope differs slightly from the atomic mass of the isotope. For instance, the isotope ^{35}Cl has an atomic mass of 34.968852 u. In fact, the *only* isotope that has an atomic mass equal to its mass number is ^{12}C, since *by definition* the mass of this atom is exactly 12 u.

Table 3.2 **Abundance of Hydrogen Isotopes**

Hydrogen Isotope	Mass	Percentage Abundance
^{1}H	1.007825 u	99.985
^{2}H	2.0140 u	0.015

Average Atomic Masses from Isotopic Abundances

Originally, the relative atomic masses of the elements were determined in a way similar to that described for hydrogen and fluorine in our earlier discussion. A sample of a compound was analyzed and from the formula of the substance the relative atomic masses were calculated. These were then adjusted to place them on the unified atomic mass scale. In modern times, methods, such as mass spectrometry discussed in On the Cutting Edge 3.1, have been developed to measure very precisely both the relative abundances of the isotopes of the elements and their atomic masses. This kind of information has made it possible to calculate more precise values of the average atomic masses, which are found in the table on the inside front cover of the book. The average atomic mass for any element can be calculated by multiplying the percentage of each isotope by its mass and adding the values together. Example 3.2 illustrates how this calculation is done.

■ Weighted averages allow you to calculate how much each isotope contributes to the overall atomic mass of the element.

Example 3.2
Calculating Average Atomic Masses from Isotopic Abundances

Naturally occurring chlorine is a mixture of two isotopes. In every sample of this element, 75.77% of the atoms are ^{35}Cl and 24.23% are atoms of ^{37}Cl. The accurately measured atomic mass of ^{35}Cl is 34.9689 u and that of ^{37}Cl is 36.9659 u. From these data, calculate the average atomic mass of chlorine.

■ **Analysis:** In a sample of chlorine, 75.77% of the mass is contributed by atoms of ^{35}Cl and 24.23% comes from atoms of ^{37}Cl. Thus, when we calculate the mass of the "average atom" we have to take into account both the masses of the isotopes and their relative abundances.

■ **Assembling the Tools:** If a sample is made up of more than one substance, then the mass contribution of one of the substances, *x,* in the sample is calculated using the equation

$$\text{Mass contribution of } x = (\text{total mass of } x) \times \frac{\text{percentage of } x}{100\%}$$

This is the tool we will use to calculate the mass contribution from each isotope toward the total mass of an average atom of Cl. For "percentage of *x*" we substitute the percent abundance of the isotope in question, and for "total mass of *x*" we substitute the mass of that isotope.

■ **Solution:** We will calculate the contribution of the 75.77% of the mass of an atom of ^{35}Cl to the total mass

$$\text{Mass contribution of } {}^{35}\text{Cl} = 34.9689 \text{ u} \times \frac{75.77\% \ {}^{35}\text{Cl}}{100\%} = 26.496 \text{ u}$$

and for the ^{37}Cl, its contribution is

$$\text{Mass contribution of } {}^{37}\text{Cl} = 36.9659 \text{ u} \times \frac{24.23\% \ {}^{37}\text{Cl}}{100\%} = 8.9568 \text{ u}$$

Now we add these contributions to give us the total mass of the "average atom."

$$26.496 \text{ u} + 8.957 \text{ u} = 35.453 \text{ u rounded to } 35.45 \text{ u}$$

Notice that in this two-step problem we kept one extra significant figure until the final rounding to four significant figures.

■ **Is the Answer Reasonable?** Once again, the final step is a check to see whether the answer makes sense. Here is how we might do such a check: First, from the masses of the isotopes, we know the average atomic mass is somewhere between approximately 35 and 37. If the abundances of the two isotopes were equal, the average would be nearly 36. However, there is more ^{35}Cl than ^{37}Cl, so a value closer to 35 than 37 seems reasonable; therefore, we can feel pretty confident our answer is correct.

Practice Exercises

3.4 | Aluminum atoms have a mass that is 2.24845 times that of an atom of ^{12}C. What is the atomic mass of aluminum? (*Hint:* Recall that we have a tool that gives the relationship between the atomic mass unit and ^{12}C.)

3.5 | How much heavier is the average atom of naturally occurring copper than an atom of ^{12}C? Refer to the table inside the front cover of the book for the necessary data.

3.6 | Naturally occurring boron is composed of 19.9% of ^{10}B and 80.1% of ^{11}B. Atoms of ^{10}B have a mass of 10.0129 u and those of ^{11}B have a mass of 11.0093 u. Calculate the average atomic mass of boron.

3.7 | Neon, the gas used in neon lamps, is composed of 90.483% of ^{20}Ne, 0.271% of ^{21}Ne, and 9.253% of ^{22}Ne. The ^{20}Ne atoms have a mass of 19.992 u, ^{21}Ne atoms have a mass of 20.994, and those of ^{22}Ne have a mass of 21.991 u. Calculate the average atomic mass of neon.

3.2 | The Periodic Table

When we study different kinds of substances, we find that some are elements and others are compounds. Among compounds, some are composed of discrete molecules. Others are *ionic compounds*, made up of atoms that have acquired electrical charges. Some elements, such as sodium, have properties we associate with metals, whereas others, such as chlorine, do not have metallic properties and are said to be nonmetallic. If we were to continue on this way, without attempting to build our subject around some central organizing structure, it would not be long before we became buried beneath a mountain of information of seemingly unconnected facts.

Mendeleev's Periodic Table

The need for organization was recognized by many early chemists, and there were numerous attempts to discover relationships among the chemical and physical properties of the elements. The periodic table we use today is based primarily on the efforts of a Russian chemist, Dmitri Ivanovich Mendeleev (1834–1907) and a German physicist, Julius Lothar Meyer (1830–1895). Working independently, these scientists developed similar periodic tables only a few months apart in 1869. Mendeleev is usually given the credit, however, because he had the good fortune to publish first.

Mendeleev was preparing a chemistry textbook for his students at the University of St. Petersburg. Looking for some pattern among the properties of the elements, he found that when he arranged them in order of increasing atomic mass, similar chemical properties were repeated over and over again at regular intervals. For instance, the elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs) are soft metals that are very reactive toward water. They form compounds with chlorine that have a 1-to-1 ratio of metal to chlorine. Similarly, the elements that immediately follow each of these also constitute a set with similar chemical properties. Thus, beryllium (Be) follows lithium, magnesium (Mg) follows sodium, calcium (Ca) follows potassium, strontium

(Sr) follows rubidium, and barium (Ba) follows cesium. All of these elements form a water-soluble chlorine compound with a 1-to-2 metal to chlorine atom ratio. Mendeleev used such observations to construct his **periodic table.**

■ Periodic refers to the recurrence of properties at regular intervals.

The elements in Mendeleev's table are arranged in order of increasing atomic mass. When the sequence is broken at the right places, the elements fall naturally into columns in which the elements in a given column have similar chemical properties. Mendeleev's genius rested on his placing elements with similar properties in the same column even when this left occasional gaps in the table. Mendeleev reasoned, correctly, that the elements that belonged in these gaps had simply not yet been discovered. In fact, on the basis of the location of these gaps, Mendeleev was able to predict with remarkable accuracy the properties of these yet-to-be-found substances. His predictions helped serve as a guide in the search for the missing elements.

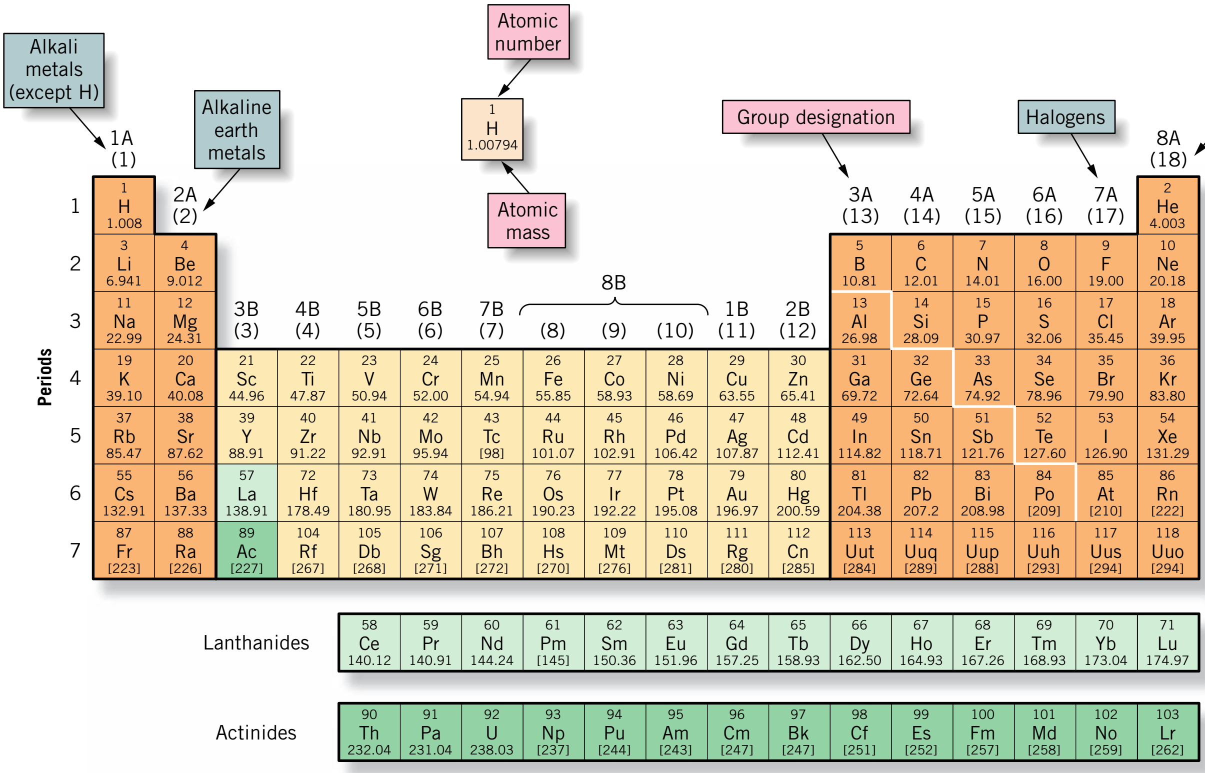
Arrangement of the Modern Periodic Table

When the concept of atomic numbers was developed, it was soon realized that the elements in Mendeleev's table were arranged in precisely the order of increasing atomic number. The fact that it is the atomic number—the number of protons in the nucleus of an atom—that determines the order of elements in the table is very significant. We will see later that this has important implications with regard to the relationship between the number of electrons in an atom and the atom's chemical properties.

The modern periodic table is shown in Figure 3.6 and also appears on the inside front cover of the book. We will refer to the table frequently, so it is important for you to become familiar with it and with some of the terminology applied to it.

TOOLS

Periodic table



Alkali metals (except H)
Alkaline earth metals
Atomic number
1
H
1.00794
Atomic mass
Group designation
Halogens
Noble gases
Periods

Periods	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	(9)	(10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [267]	105 Db [268]	106 Sg [271]	107 Bh [272]	108 Hs [270]	109 Mt [276]	110 Ds [281]	111 Rg [280]	112 Cn [285]	113 Uut [284]	114 Uuq [289]	115 Uup [288]	116 Uuh [293]	117 Uus [294]	118 Uuo [294]

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Figure 3.6 | **The modern periodic table.** At room temperature, mercury and bromine are liquids. Eleven elements are gases, including the noble gases and the diatomic gases of hydrogen, oxygen, nitrogen, fluorine, and chlorine. The remaining elements are solids.

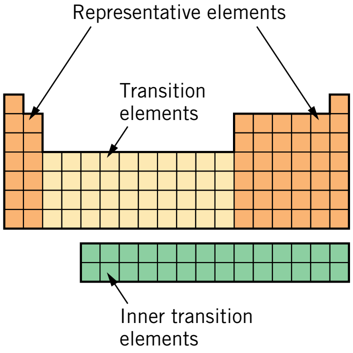
Special Terminology of the Periodic Table

In the modern periodic table the elements are arranged in order of increasing atomic number. The rows in the table are called **periods**, and for identification purposes the periods are numbered. Below the main body of the table are two long rows of 14 elements each. These actually belong in the main body of the table following La ($Z = 57$) and Ac ($Z = 89$), as shown in Figure 3.7. They are almost always placed below the table simply to conserve space. If the fully spread-out table is printed on one page, the type is so small that it's difficult to read. Notice that in the fully extended form of the table, with all the elements arranged in their proper locations, there is a great deal of empty space. An important requirement of a detailed atomic theory, which we will get to in Chapter 8, is that it must explain not only the repetition of properties, but also why there is so much empty space in the table.

■ Recall that the symbol *Z* stands for atomic number.

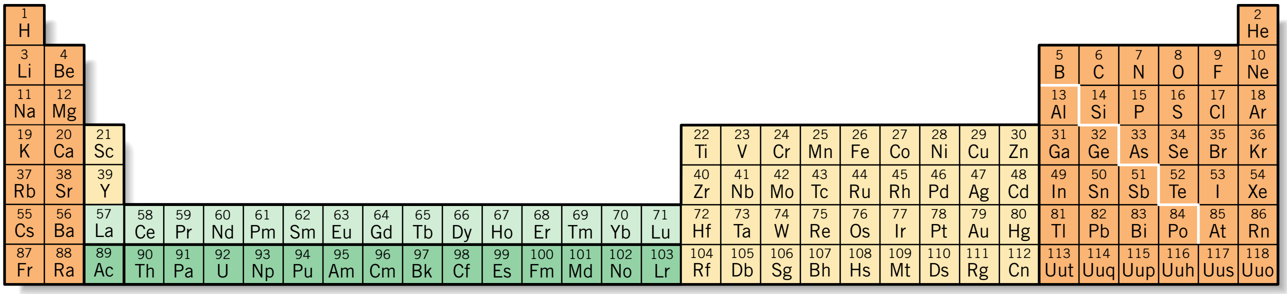
The vertical columns in the periodic table are called **groups,** also identified by numbers. However, there is not uniform agreement among chemists on the numbering system. In an attempt to standardize the table, the International Union of Pure and Applied Chemistry (the IUPAC), an international body of scientists responsible for setting standards in chemistry, officially adopted a system in which the groups are simply numbered sequentially, 1 through 18, from left to right using Arabic numerals. Chemists in North America favor the system where the longer groups are labeled 1A to 8A and the shorter groups are labeled 1B to 8B in the sequence depicted in Figure 3.6. (In some texts, groups are identified with Roman numerals; Group 3A appears as Group IIIA, for example.) Note that Group 8B actually encompasses three short columns. The sequence of the B-group elements is unique and will make sense when we learn more about the structure of the atom in Chapter 8. Additionally, European chemists favor a third numbering system with the designation of A and B groups but with a different sequence from the North American table.

In Figure 3.6 and on the inside front cover of the book, we have used both the North American labels as well as those preferred by the IUPAC. Because of the lack of uniform agreement among chemists on how the groups should be specified, we will use the North American A-group/B-group designations in Figure 3.6 when we wish to specify a particular group.



As we have already noted, the elements in a given group bear similarities to each other. Because of such similarities, groups are sometimes referred to as **families of elements**. The elements in the longer columns (the A groups) are known as the **representative elements** or **main group elements.** Those that fall into the B groups in the center of the table are called **transition elements.** The elements in the two long rows below the main body of the table are the **inner transition elements,** and each row is named after the element that it follows in the main body of the table. Thus, elements 58–71 are called the **lanthanide elements** because they follow lanthanum ($Z = 57$), and elements 90–103 are called the **actinide elements** because they follow actinium ($Z = 89$).

Some of the groups have acquired common names. For example, except for hydrogen, the Group 1A elements are metals. They form compounds with oxygen that dissolve in water to give solutions that are strongly alkaline, or caustic. As a result, they are called the



1 H																															2 He
3 Li	4 Be																									5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg																									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc															22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y															40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Figure 3.7 | **Extended form of the periodic table.** The two long rows of elements below the main body of the table in Figure 3.6 are placed in their proper places in this table.

alkali metals or simply the *alkalis*. The Group 2A elements are also metals. Their oxygen compounds are alkaline, too, but many compounds of the Group 2A elements are unable to dissolve in water and are found in deposits in the ground. Because of their properties and where they occur in nature, the Group 2A elements became known as the **alkaline earth metals.**

On the right side of the table, in Group 8A, are the **noble gases**. They used to be called the inert gases until it was discovered that the heavier members of the group show a small degree of chemical reactivity. The term *noble* is used when we wish to suggest a very limited degree of chemical reactivity. Gold, for instance, is often referred to as a noble metal because so few chemicals are capable of reacting with it.

Finally, the elements of Group 7A are called the **halogens,** derived from the Greek word meaning "sea" or "salt." Chlorine (Cl), for example, is found in familiar table salt, a compound that accounts in large measure for the salty taste of seawater. The other groups of the representative elements have less frequently used names, and we will name those groups based on the first element in the family. For example, Group 5A is the **nitrogen family**.

■ The Group 6A elements are also called the *chalcogens*, and the Group 5A elements are also called the *pnictogens*.

3.3 | Metals, Nonmetals, and Metalloids

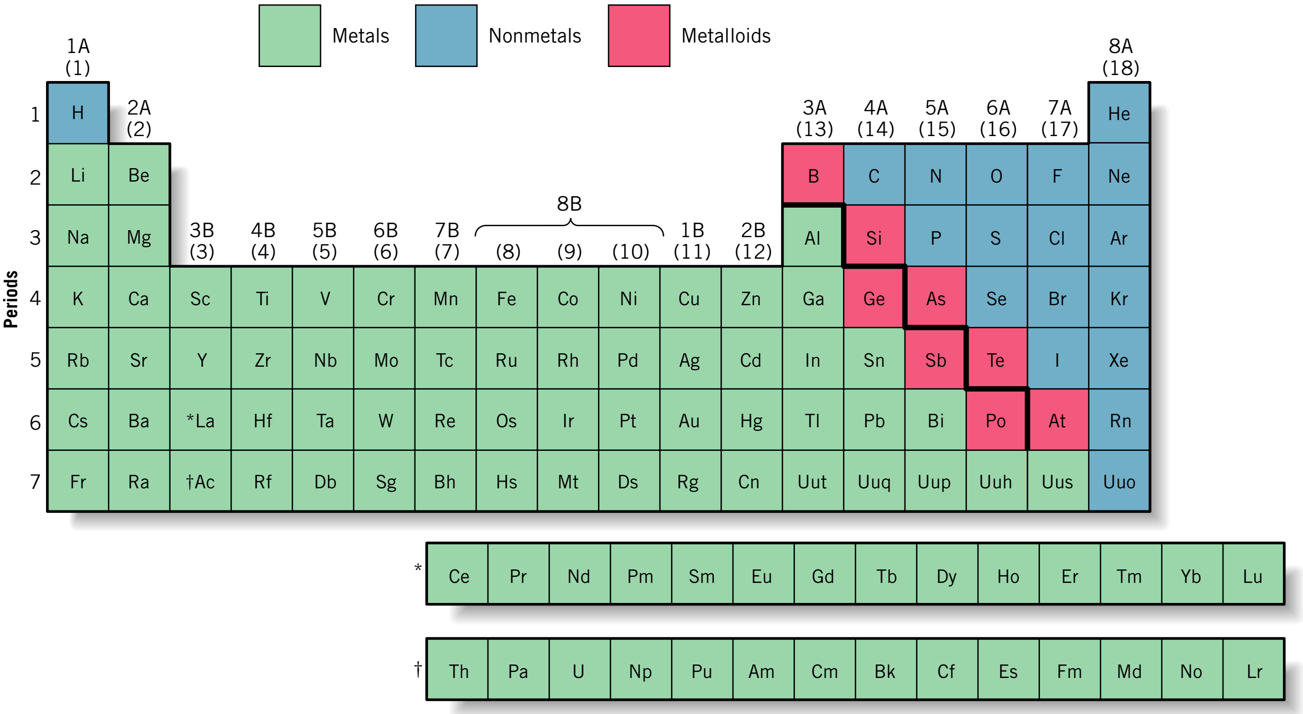
The periodic table organizes all sorts of chemical and physical information about the elements and their compounds. It allows us to study systematically the way properties vary with an element's position within the table and, in turn, makes the similarities and differences among the elements easier to understand and remember.

Even a casual inspection of samples of the elements reveals that some are familiar metals and that others, equally well known, are not metals. Most of us recognize metals such as lead, iron, or gold and nonmetals such as oxygen or nitrogen. A closer look at the nonmetallic elements, though, reveals that some of them, silicon and arsenic to name two, have properties that lie between those of true metals and true nonmetals. These elements are called **metalloids.** The elements are not evenly divided into the categories of metals, nonmetals, and metalloids. (See Figure 3.8.) Most elements are metals, slightly over a dozen are nonmetals, and only a handful are metalloids.

TOOLS

Periodic table: metals, nonmetals, and metalloids

■ The metalloids are grouped around the bold stair-step line that is drawn diagonally from boron (B) down to astatine (At).



🟩 Metals 🟦 Nonmetals 🟥 Metalloids

Periods	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	†Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 3.8 | **Distribution of metals, nonmetals, and metalloids among the elements in the periodic table.**

Metals

TOOLS Properties of metals

You probably know a **metal** when you see one, and you are familiar with their physical properties. Metals tend to have a shine so unique that it's called a *metallic luster*. For example, the silvery sheen of the surface of potassium in Figure 3.9 would most likely lead you to identify potassium as a metal even if you had never seen or heard of it before. We also know that metals conduct electricity. Few of us would hold an iron nail in our hand and poke it into an electrical outlet. In addition, we know that metals conduct heat very well. On a cool day, metals always feel colder to the touch than do neighboring nonmetallic objects because metals conduct heat away from your hand very rapidly. Nonmetals seem less cold because they can't conduct heat away as quickly and therefore their surfaces warm up faster.

Other properties that metals possess, to varying degrees, are **malleability**—the ability to be hammered or rolled into thin sheets—and **ductility**—the ability to be drawn into wire. The ability of gold to be hammered into foils a few atoms thick depends on the malleability of gold (Figure 3.10), and the manufacture of electrical wire is based on the ductility of copper.

■ Thin lead sheets are used for sound deadening because the easily deformed lead absorbs the sound vibrations.

Hardness is another physical property that we usually think of for metals. Some, such as chromium or iron, are indeed quite hard; but others, including copper and lead, are rather soft. The alkali metals such as potassium (Figure 3.9) are so soft they can be cut with a knife, but they are also so chemically reactive that we rarely get to see them as free elements.

All the metallic elements, except mercury, are solids at room temperature (Figure 3.11). Mercury's low freezing point (−39 °C) and fairly high boiling point (357 °C) make it useful as a fluid in thermometers. Most of the other metals have much higher melting points. Tungsten, for example, has the highest melting point of any metal (3400 °C, or 6150 °F), which explains its use as filaments that glow white-hot in electric lightbulbs.

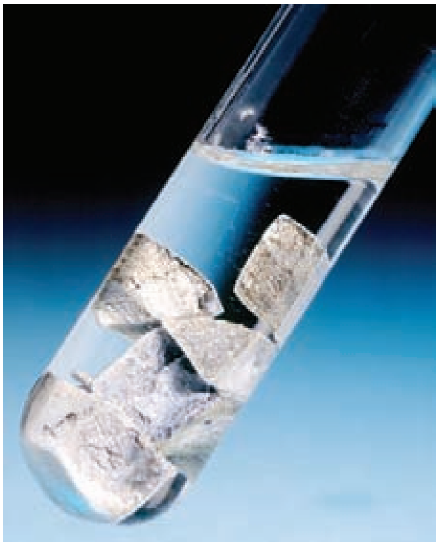


Figure 3.9 | **Potassium is a metal.** Potassium reacts quickly with moisture and oxygen to form a white coating. Due to its high reactivity, it is stored under oil to prevent water and oxygen from reacting with it. *(© 1995 Richard Megna/Fundamental Photographs)*

Figure 3.10 | **Malleability of gold.** Pure gold is not usually used in jewelry because it is too malleable. It is used decoratively to cover domes since it can be hammered into very thin sheets called gold leaf. *(Joseph Sohm; Visions of America/©Corbis)*

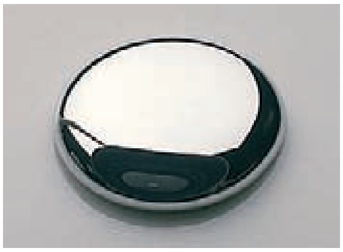


Figure 3.11 | **Mercury droplet.** The metal mercury (once known as quicksilver) is a liquid at room temperature, unlike other metals, which are solids. *(OPC, Inc.)*

The chemical properties of metals vary tremendously. Some, such as gold and platinum, are very unreactive toward almost all chemical agents. This property, plus their natural beauty and rarity, makes them highly prized for use in jewelry. Other metals, however, are so reactive that few people except chemists and chemistry students ever get to see them in their "free" states. For instance, the metal sodium reacts very quickly with oxygen or moisture in the air, and its bright metallic surface tarnishes almost immediately.

■ We use the term "free element" to mean an element that is not chemically combined with any other element.

Nonmetals

Substances such as plastics, wood, and glass that lack the properties of metals are said to be *nonmetallic*, and an element that has nonmetallic properties is called a **nonmetal**. Most often, we encounter the nonmetals in the form of compounds or mixtures of compounds. There are some nonmetals, however, that are very important to us in their elemental forms. The air we breathe, for instance, contains mostly nitrogen and oxygen. Both are gaseous, colorless, and odorless nonmetals. Since we can't see, taste, or smell them, however, it's difficult to experience their existence. (Although if you step into an atmosphere without oxygen, your body will soon tell you that something is missing!) Probably the most commonly *observed* nonmetallic element is carbon. We find it as the graphite in pencils, as coal, and as the charcoal used for barbecues. It also occurs in a more valuable form as diamond (Figure 3.12). Although diamond and graphite differ in appearance, each is a form of elemental carbon.

Many of the nonmetals are solids at room temperature and atmospheric pressure, while many others are gases. Photographs of some of the nonmetallic elements appear in Figure 3.13. Their properties are almost completely opposite those of metals. Each of these elements lacks the characteristic appearance of a metal. They are poor conductors of heat and, with the exception of the graphite form of carbon, are also poor conductors of electricity. The electrical conductivity of graphite appears to be an accident of molecular structure, since the structures of metals and graphite are completely different.

Figure 3.12 | **Diamonds.** Gems such as these are simply another form of the element carbon. *(Charles D. Winters/Photo Researchers, Inc.)*

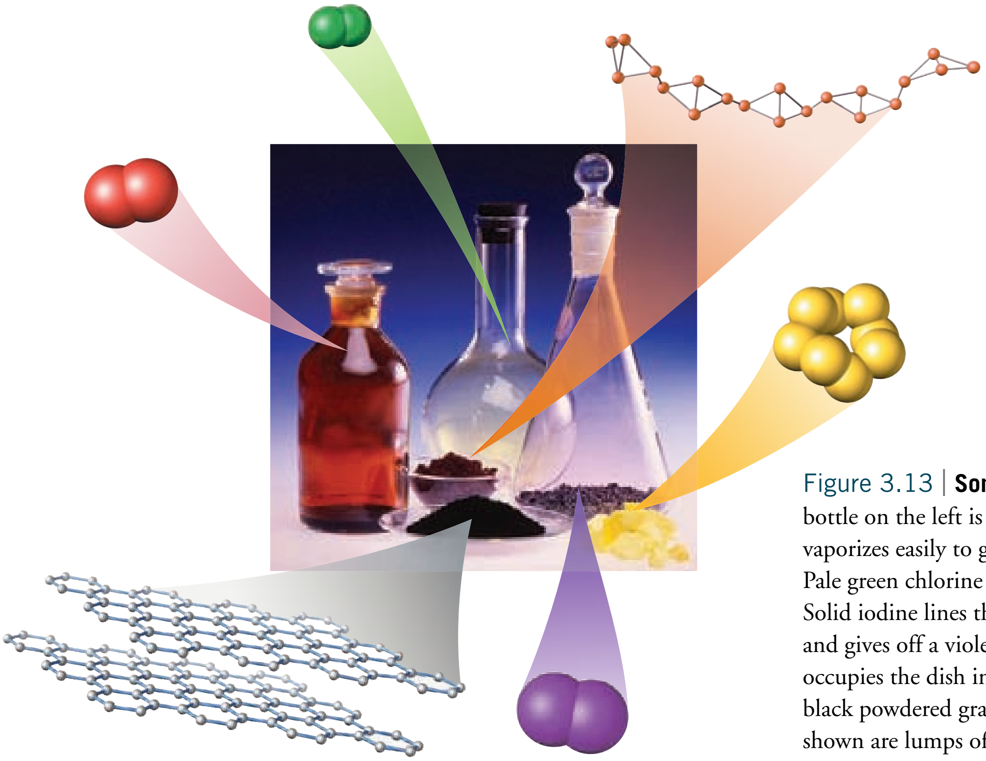


Figure 3.13 | **Some nonmetallic elements.** In the bottle on the left is dark-red liquid bromine, which vaporizes easily to give a deeply colored orange vapor. Pale green chlorine fills the round flask in the center. Solid iodine lines the bottom of the flask on the right and gives off a violet vapor. Powdered red phosphorus occupies the dish in front of the flask of chlorine, and black powdered graphite is in the watch glass. Also shown are lumps of yellow sulfur. *(Michael Watson)*

The nonmetallic elements lack the malleability and ductility of metals. A lump of sulfur crumbles when hammered and breaks apart when pulled on. Diamond cutters rely on the brittle nature of carbon when they split a gem-quality stone by carefully striking a quick blow with a sharp blade.

As with metals, nonmetals exhibit a broad range of chemical reactivities. Fluorine, for instance, is extremely reactive. It reacts readily with almost all of the other elements. At the other extreme is helium, the gas used to inflate children's balloons and the blimps seen at major sporting events. This element does not react with anything, a fact that chemists find useful when they want to provide a totally *inert* (unreactive) atmosphere inside some apparatus.

Metalloids

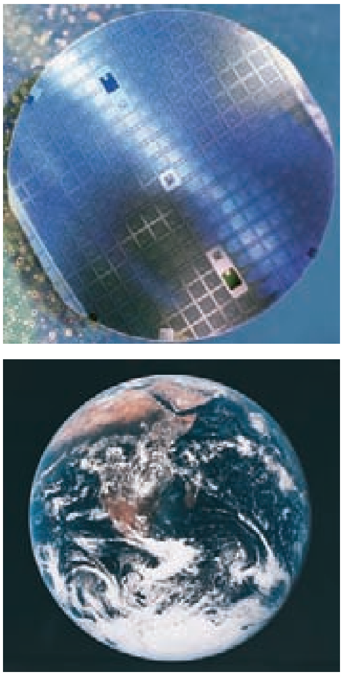


Figure 3.14 | **Modern electronic circuits rely on the semiconductor properties of silicon.** The silicon wafer shown here contains more electronic components (10 billion) than there are people on our entire planet (about 6.5 billion)! *(Courtesy NASA)*

The properties of metalloids lie between those of metals and nonmetals. This shouldn't surprise us since the metalloids are located between the metals and the nonmetals in the periodic table. In most respects, metalloids behave as nonmetals, both chemically and physically. However, in their most important physical property, electrical conductivity, they somewhat resemble metals. Metalloids tend to be **semiconductors**; they conduct electricity, but not nearly as well as metals. This property, particularly as found in silicon and germanium, is responsible for the remarkable progress made during the last five decades in the field of solid-state electronics. The operation of every computer, audio system, TV receiver, DVD or CD player, and AM-FM radio relies on transistors made from semiconductors. Perhaps the most amazing advance of all has been the fantastic reduction in the size of electronic components that semiconductors have allowed (Figure 3.14). To it, we owe the development of small and versatile cell phones, cameras, flash drives, MP3 players, calculators, and computers. The heart of these devices is an integrated circuit that begins as a wafer of extremely pure silicon (or germanium) that is etched and chemically modified into specialized arrays of thousands of transistors.

Metallic and Nonmetallic Character

The occurrence of the metalloids between the metals and the nonmetals is our first example of trends in properties within the periodic table. We will frequently see that as we move from position to position across a period or down a group in the table, chemical and physical properties change in a gradual way. There are few abrupt changes in the characteristics of the elements as we scan across a period or down a group. The location of the metalloids can be seen, then, as an example of the gradual transition between metallic and nonmetallic properties. From left to right across Period 3, we go from aluminum, an element that has every appearance of a metal; to silicon, a semiconductor; to phosphorus, an element with clearly nonmetallic properties. A similar gradual change is seen going down Group 4A. Carbon is a nonmetal, silicon and germanium are metalloids, and tin and lead are metals. Trends such as these are useful to spot because they help us remember properties.

3.4 | Ionic Compounds

Most of the substances that we encounter on a daily basis are not free elements but are compounds in which the elements are combined with each other. We will discuss two types of compounds: ionic and molecular.

Reactions of Metals with Nonmetals

Under appropriate conditions, atoms are able to transfer electrons between one another when they react to yield electrically charged particles called **ions**. This is what happens, for example, when the metal sodium combines with the nonmetal chlorine. As shown in Figure 3.15, when sodium, a typical shiny metal, and chlorine, a pale green gas, are mixed, a vigorous reaction takes place yielding a white powder, sodium chloride. The equation for the reaction is

$$2\mathrm{Na}(s) + \mathrm{Cl}_2(g) \longrightarrow 2\mathrm{NaCl}(s)$$

The changes that take place at the atomic level are also illustrated in Figure 3.15.

The formation of the ions in sodium chloride results from the transfer of electrons between the reacting atoms. Specifically, each sodium atom gives up one electron to a chlorine atom. We can diagram the changes in equation form by using the symbol e^- to stand for an electron.

$$\overset{\overset{e^-}{\curvearrowright}}{\mathrm{Na} + \mathrm{Cl}} \longrightarrow \mathrm{Na}^+ + \mathrm{Cl}^-$$

■ Here we are concentrating on what happens to the individual atoms, so we have not shown chlorine as diatomic Cl_2 molecules.

The electrically charged particles formed in this reaction are a sodium ion (Na^+) and a chloride ion (Cl^-). The sodium ion has a positive 1+ charge, indicated by the superscript plus sign, because the loss of an electron leaves it with one more proton in its nucleus than there are electrons outside. Similarly, by gaining one electron the chlorine atom has added one more negative charge, so the chloride ion has a single negative charge indicated by the minus sign. Solid sodium chloride is composed of these charged sodium and chloride ions and is said to be an **ionic compound**.

■ A neutral sodium atom has 11 protons and 11 electrons; a sodium ion has 11 protons and 10 electrons, so it carries a unit positive charge. A neutral chlorine atom has 17 protons and 17 electrons; a chloride ion has 17 protons and 18 electrons, so it carries a unit negative charge.

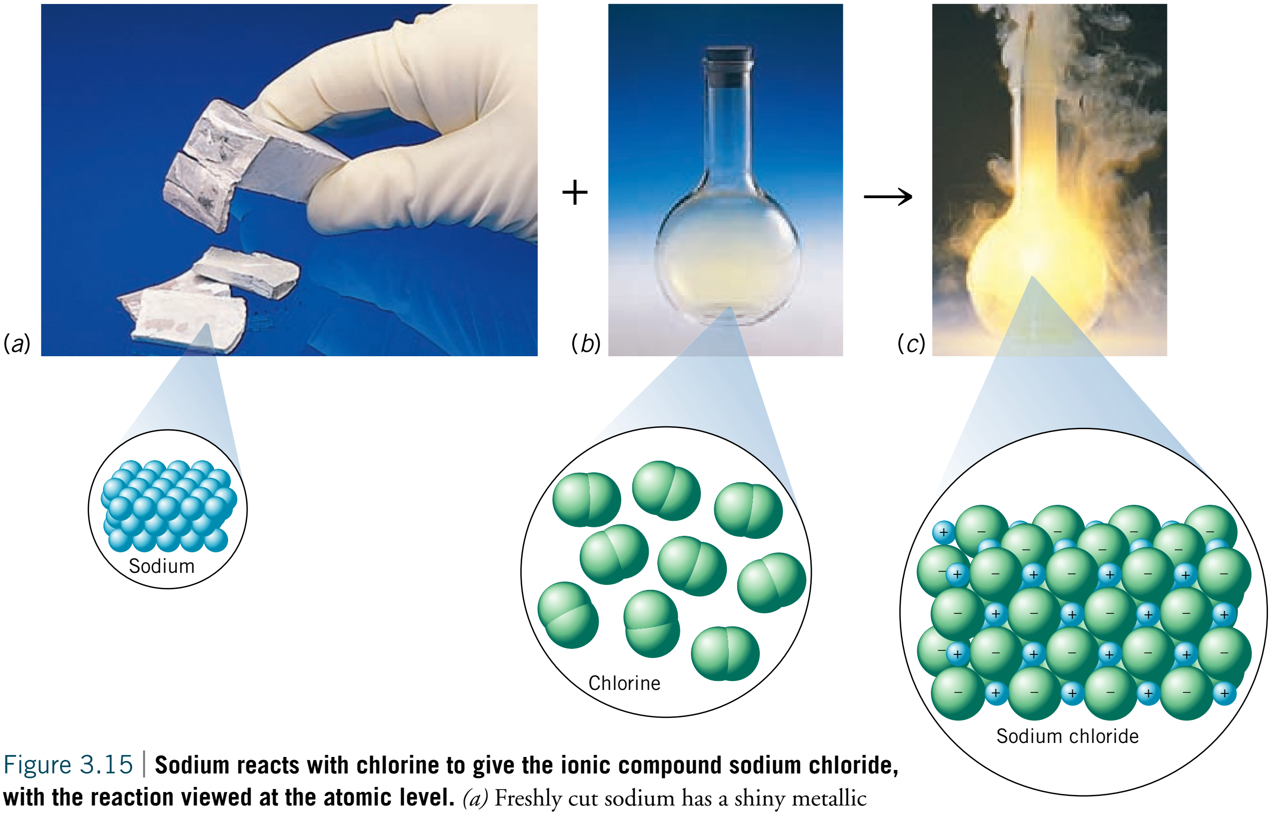


Figure 3.15 | **Sodium reacts with chlorine to give the ionic compound sodium chloride, with the reaction viewed at the atomic level.** *(a)* Freshly cut sodium has a shiny metallic surface. The metal reacts with oxygen and moisture, so it cannot be touched with bare fingers. *(b)* Chlorine is a pale green gas. *(c)* When a small piece of sodium is melted in a metal spoon and thrust into the flask of chlorine, it burns brightly as the two elements react to form sodium chloride. The smoke coming from the flask is composed of fine crystals of salt. The electrically neutral atoms and molecules react to yield positive and negative ions, which are held to each other by electrostatic attractions (attractions between opposite electrical charges). *(Michael Watson; Richard Megna/Fundamental Photographs; Richard Megna/Fundamental Photographs)*

TOOLS Ionic compounds

As a general rule, *ionic compounds are formed when metals react with nonmetals*. In the electron transfer, however, not all atoms gain or lose just one electron; some gain or lose more. For example, when calcium atoms react they lose two electrons to form Ca^{2+} ions, and when oxygen atoms form ions they each gain two electrons to give O^{2-} ions. Notice that in writing the formulas for ions, the number of positive or negative charges is indicated by a superscript before the positive or negative charge. (We will have to wait until a later chapter to study the reasons why certain atoms gain or lose one electron each, whereas other atoms gain or lose two or more electrons.)

Practice Exercises

3.8 | For each of the following atoms or ions, give the number of protons and the number of electrons in one particle: (a) an Fe atom, (b) an Fe^{3+} ion, (c) an N^{3-} ion, (d) an N atom. (*Hint:* Recall that electrons have a negative charge and ions that have a negative charge must have gained electrons.)

3.9 | For each of the following atoms or ions, give the number of protons and the number of electrons in one particle: (a) an O atom, (b) an O^{2-} ion, (c) an Al^{3+} ion, (d) an Al atom.

Looking at the structure of sodium chloride in Figure 3.15, it is impossible to say that a particular Na^+ ion belongs to a particular Cl^- ion. The ions in a crystal of NaCl are simply packed in the most efficient way, so that positive ions and negative ions can be as close to each other as possible. In this way, the attractions between oppositely charged ions, which are responsible for holding the compound together, can be as strong as possible.

■ The charges on the ions are omitted when writing formulas for compounds because compounds are electrically neutral overall.

Since discrete units don't exist in ionic compounds, the subscripts in their formulas are always chosen to specify the smallest whole-number ratio of the ions. This is why the formula of sodium chloride is given as NaCl rather than Na_2Cl_2 or Na_3Cl_3. The idea of a "smallest unit" of an ionic compound is still quite often useful. Therefore, we take the smallest unit of an ionic compound to be whatever is represented in its formula and call this unit a **formula unit.** Thus, one formula unit of NaCl consists of one Na^+ and one Cl^-, whereas one formula unit of the ionic compound $CaCl_2$ consists of one Ca^{2+} and two Cl^- ions. (In a broader sense, we can use the term *formula unit* to refer to whatever is represented by a formula. Sometimes the formula specifies a set of ions, as in NaCl; sometimes it is a molecule, as in O_2 or H_2O; sometimes it can be just an ion, as in Cl^- or Ca^{2+}; and sometimes it might be just an atom, as in Na.)

Experimental Evidence Exists for Ions in Compounds

We know that metals conduct electricity because electrons can move from one atom to the next in a wire when connected to a battery. Solid ionic compounds are poor conductors of electricity as are other substances such as water. However, if an ionic compound is dissolved in water or is heated to a high temperature so that it melts, the resulting liquids are able to conduct electricity easily. These observations suggest that ionic compounds are composed of charged ions rather than neutral molecules and that these ions when made mobile by dissolving or melting can conduct electricity. Figure 3.16 illustrates how the electrical conductivity can be tested.

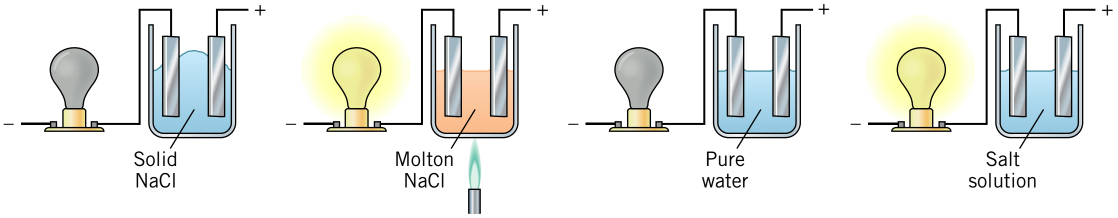


Figure 3.16 | **An apparatus to test for electrical conductivity.** The electrodes are dipped into the substance to be tested. If the lightbulb glows when electricity is applied, the sample is an electrical conductor. Here we see that solid sodium chloride does not conduct electricity, but when the solid is melted it does conduct. Liquid water, a molecular compound, is not a conductor of electricity because it does not contain electrically charged particles.

Formulas of Ionic Compounds

We have noted that metals combine with nonmetals to form ionic compounds. In such reactions, metal atoms lose one or more electrons to become positively charged ions and nonmetal atoms gain one or more electrons to become negatively charged ions. In referring to these particles, a positively charged ion is called a **cation** (pronounced *CAT-i-on)* and a negatively charged ion is called an **anion** (pronounced *AN-i-on*).[1] Thus, solid NaCl is composed of sodium cations and chloride anions.

Ions of Representative Metals and Nonmetals

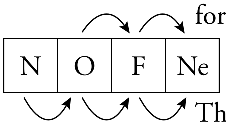
The periodic table can help us remember the kinds of ions formed by many of the representative elements (elements in the A-groups of the periodic table). For example, except for hydrogen, the neutral atoms of the Group 1A elements always lose one electron each when they react, thereby becoming ions with a charge of 1+. Similarly, atoms of the Group 2A elements always lose two electrons when they react, so these elements always form ions with a charge of 2+. In Group 3A, the only important positive ion we need consider now is that of aluminum, Al^{3+}; an aluminum atom loses three electrons when it reacts to form this ion.

All these ions are listed in Table 3.3. *Notice that the number of positive charges on each of the cations is the same as the group number when we use the North American numbering of the groups in the periodic table.* Thus, sodium is in Group 1A and forms an ion with a 1+ charge, barium (Ba) is in Group 2A and forms an ion with a 2+ charge, and aluminum is in Group 3A and forms an ion with a 3+ charge. Although this generalization doesn't work for all the metallic elements (for example, the transition elements), it does help us remember what happens to the metallic elements of Groups 1A and 2A and aluminum when they react.

TOOLS
Predicting cation charge

Among the nonmetals on the right side of the periodic table we also find some useful generalizations. For example, when they combine with metals, the halogens (Group 7A) form ions with one negative charge (written as 1−) and the nonmetals in Group 6A form ions with two negative charges (written as 2−). Notice that *the number of negative charges on the anion is equal to the number of spaces to the right that we have to move in the periodic table to get to a noble gas.*

TOOLS
Predicting anion charge



Two steps, so oxygen forms O^{2-}.

Three steps, so nitrogen forms N^{3-}.

Table 3.3 **Some Ions Formed from the Representative Elements**

Group Number						
1A	**2A**	**3A**	**4A**	**5A**	**6A**	**7A**
H^+						
Li^+	Be^{2+}		C^{4-}	N^{3-}	O^{2-}	F^-
Na^+	Mg^{2+}	Al^{3+}	Si^{4-}	P^{3-}	S^{2-}	Cl^-
K^+	Ca^{2+}				Se^{2-}	Br^-
Rb^+	Sr^{2+}				Te^{2-}	I^-
Cs^+	Ba^{2+}					

---

[1] The names *cation* and *anion* come from the way the ions behave when electrically charged metal plates called electrodes are dipped into a solution that contains them. We will discuss this in detail in Chapter 20.

Writing Formulas for Ionic Compounds

A substance is electrically neutral, with a net charge of zero, if the total positive charge equals the total negative charge.

All chemical compounds are electrically neutral, so the ions in an ionic compound always occur in a ratio such that the total positive charge is equal to the total negative charge. This is why the formula for sodium chloride is NaCl; the 1-to-1 ratio of Na^+ to Cl^- gives electrical neutrality. In addition, as we've already mentioned, discrete molecules do not exist in ionic compounds, so we always use the smallest set of subscripts that specify the correct ratio of the ions. The following, therefore, are the rules we use in writing the formulas of ionic compounds.

TOOLS Formulas for ionic compounds

Rules for Writing Formulas of Ionic Compounds

1. The positive ion is given first in the formula. (This isn't required by nature, but it is a custom we always follow.)
2. The subscripts in the formula must produce an electrically neutral formula unit. (Nature *does* require electrical neutrality.)
3. The subscripts should be the smallest set of whole numbers possible. For instance, if all subscripts are even, divide them by 2. (You may have to repeat this simplification step several times.)
4. The charges on the ions are not included in the finished formula for the substance. When a subscript is 1 it is left off; no subscript implies a subscript of 1.

Example 3.3
Writing Formulas for Ionic Compounds

Write the formulas for the ionic compounds formed from (a) Ba and S, (b) Al and Cl, and (c) Al and O.

Analysis: To correctly write the formula, determine the charges on the anion and the cation and then follow the rules for writing ionic compounds listed above.

Assembling the Tools: First, we need the tool to figure out the charges of the ions from the periodic table. Then we apply the tool that summarizes the rules for writing the formula of ionic compounds.

Solution:

(a) The element Ba is in Group 2A, so the charge on its ion is 2+. Sulfur is in Group 6A, so its ion has a charge of 2−. Therefore, the ions are Ba^{2+} and S^{2-}. Since the charges are equal but opposite, a 1-to-1 ratio will give a neutral formula unit. Therefore, the formula is BaS. Notice that we have *not* included the charges on the ions in the finished formula.

(b) By using the periodic table, the ions of these elements are Al^{3+} and Cl^-. We can obtain a neutral formula unit by combining one Al^{3+} with three Cl^-. (The charge on Cl is 1−; the 1 is understood.)

$$1(3+) + 3(1-) = 0$$

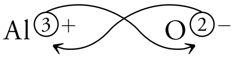
The formula is $AlCl_3$.

(c) For these elements, the ions are Al^{3+} and O^{2-}. In the formula we seek there must be the same number of positive charges as negative charges. This number must be a whole-number multiple of both 3 and 2. The smallest number that satisfies this condition is 6, so there must be two Al^{3+} and three O^{2-} in the formula.

$$\begin{array}{ll} 2Al^{3+} & 2(3+) = 6+ \\ 3O^{2-} & \underline{3(2-) = 6-} \\ & \text{sum} = 0 \end{array}$$

The formula is Al_2O_3.

A "trick" you may have seen before is to use the *number* of positive charges for the subscript of the anion and the *number* of negative charges as the subscript for the cation as shown in the diagram.



When using this method, always be sure to check that the subscripts cannot be reduced to smaller numbers.

■ **Are the Answers Reasonable?** In writing a formula, there are two things to check. First, be sure you've correctly written the formulas of the ions. (This is often the main reason for a lot of mistakes.) Then check that you've combined them in a ratio that gives electrical neutrality. Performing these checks assures us we've got the right answers.

Practice Exercises

3.10 | Write formulas for ionic compounds formed from (a) Na and F, (b) Na and O, (c) Mg and F, and (d) Al and C. (*Hint:* One element must form a cation, and the other will form an anion based on its position in the periodic table.)

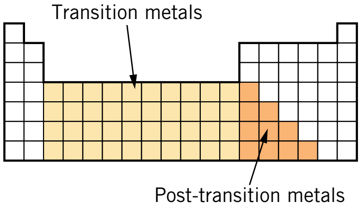
3.11 | Write the formulas for the compounds made from (a) Ca and N, (b) Al and Br, (c) K and S, (d) Cs and Cl.

Many of our most important chemicals are ionic compounds. We have mentioned NaCl, common table salt, and $CaCl_2$, which is a substance often used to melt ice on walkways in the winter. Other examples are sodium fluoride, NaF, used by dentists to give fluoride treatments to teeth, and calcium oxide, CaO, an important ingredient in cement.

Cations of Transition and Post-transition Metals

The transition elements are located in the center of the periodic table, from Group 3B on the left to Group 2B on the right (Groups 3 to 12 if using the IUPAC system). All of them lie to the left of the metalloids, and they all are metals. Included here are some of our most familiar metals, including iron, chromium, copper, silver, and gold.

Most of the transition metals are much less reactive than the metals of Groups 1A and 2A, but when they react they also transfer electrons to nonmetal atoms to form ionic compounds. However, the charges on the ions of the transition metals do not follow as straightforward a pattern as do those of the alkali and alkaline earth metals. One of the characteristic features of the transition metals is the ability of many of them to form more than one positive ion. Iron, for example, can form two different ions, Fe^{2+} and Fe^{3+}. This means that iron can form more than one compound with a given nonmetal. For example, with chloride ion, Cl^-, iron forms two compounds, with the formulas $FeCl_2$ and $FeCl_3$. With oxygen, we find the compounds FeO and Fe_2O_3. As usual, we see that the formulas contain the ions in a ratio that gives electrical neutrality. Some of the most common ions of the transition metals are given in Table 3.4. Notice that one of the ions of mercury is diatomic $Hg_2{}^{2+}$. It consists of two Hg^+ ions joined by the same kind of bond found in molecular substances. The simple Hg^+ ion does not exist.



Distribution of transition and post-transition metals in the periodic table.

Practice Exercises

3.12 | Write formulas for the chlorides and oxides formed by (a) chromium and (b) copper. (*Hint:* There are more than one chloride and one oxide for each of these transition metals.)

3.13 | Write the formulas for the sulfides and nitrides of (a) gold and (b) titanium.

The **post-transition metals** are those metals that occur in the periodic table immediately following a row of transition metals. The two most common and important ones are tin (Sn) and lead (Pb). Except for bismuth, post-transition metals have the ability to form two

■ The prefix *post* means "after."

different ions and therefore two different compounds with a given nonmetal. For example, tin forms two oxides, SnO and SnO_2. Lead also forms two oxides that have similar formulas (PbO and PbO_2). The ions that these metals form are also included in Table 3.4.

Compounds Containing Polyatomic Ions

TOOLS Polyatomic ions

The ionic compounds that we have discussed so far have been **binary compounds**—compounds formed from *two* different elements. There are many other ionic compounds that contain more than two elements. These substances usually contain **polyatomic ions,** which are ions that are themselves composed of two or more atoms linked by the same kinds of bonds that hold molecules together. Polyatomic ions differ from molecules, however, in that they contain either too many or too few electrons to make them electrically neutral. Table 3.5 lists some important polyatomic ions. It is very important that you learn the formulas, charges, and names of all of these ions.

The formulas of compounds formed from polyatomic ions are determined in the same way as are those of binary ionic compounds: the ratio of the ions must be such that the formula unit is electrically neutral, and the smallest set of whole-number subscripts is used. One difference in writing formulas with polyatomic ions is that parentheses are needed around the polyatomic ion if a subscript is required.

■ A substance is **diatomic** if it is composed of molecules that contain only two atoms. It is a **binary compound** if it contains two different elements, regardless of the number of each. Thus, $BrCl$ is a binary compound and is also diatomic; CH_4 is a binary compound but is not diatomic.

Table 3.4 Ions of Some Transition Metals and Post-transition Metals

Transition Metals	
Titanium	Ti^{2+}, Ti^{3+}, Ti^{4+}
Chromium	Cr^{2+}, Cr^{3+}
Manganese	Mn^{2+}, Mn^{3+}
Iron	Fe^{2+}, Fe^{3+}
Cobalt	Co^{2+}, Co^{3+}
Nickel	Ni^{2+}
Copper	Cu^{+}, Cu^{2+}
Zinc	Zn^{2+}
Silver	Ag^{+}
Cadmium	Cd^{2+}
Gold	Au^{+}, Au^{3+}
Mercury	Hg_2^{2+}, Hg^{2+}
Post-transition Metals	
Tin	Sn^{2+}, Sn^{4+}
Lead	Pb^{2+}, Pb^{4+}
Bismuth	Bi^{3+}

Table 3.5 Formulas and Names of Some Polyatomic Ions

Ion	Name (Alternate Name in Parentheses)
NH_4^+	Ammonium ion
H_3O^+	Hydronium ion[a]
OH^-	Hydroxide ion
CN^-	Cyanide ion
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
ClO^- or OCl^-	Hypochlorite ion
ClO_2^-	Chlorite ion
ClO_3^-	Chlorate ion
ClO_4^-	Perchlorate ion
MnO_4^-	Permanganate ion
$C_2H_3O_2^-$	Acetate ion
$C_2O_4^{2-}$	Oxalate ion
CO_3^{2-}	Carbonate ion
HCO_3^-	Hydrogen carbonate ion (bicarbonate ion)[b]
SO_3^{2-}	Sulfite ion
HSO_3^-	Hydrogen sulfite ion (bisulfite ion)[b]
SO_4^{2-}	Sulfate ion
HSO_4^-	Hydrogen sulfate ion (bisulfate ion)[b]
SCN^-	Thiocyanate ion
$S_2O_3^{2-}$	Thiosulfate ion
CrO_4^{2-}	Chromate ion
$Cr_2O_7^{2-}$	Dichromate ion
PO_4^{3-}	Phosphate ion
HPO_4^{2-}	Monohydrogen phosphate ion
$H_2PO_4^-$	Dihydrogen phosphate ion

[a] You will only encounter this ion in aqueous solutions.

[b] You will often see and hear the alternate names for these ions.

■ In general, polyatomic ions are not formed by the direct combination of elements. They are the products of reactions between compounds.

Example 3.4
Formulas That Contain Polyatomic Ions

One of the minerals responsible for the strength of bones is the ionic compound calcium phosphate, which is formed from Ca^{2+} and PO_4^{3-}. Write the formula for this compound.

Analysis: The problem is asking for the formula of an ionic compound that contains a polyatomic ion. While much information about ions relates to the periodic table, the names and formula for the polyatomic ions must be memorized.

Assembling the Tools: The essential tool for solving this problem is to follow the rules for writing formulas, paying special attention to the requirement that the compound be electrically neutral, which means that we have to balance the positive and negative charges.

Solution: Since the formula must be neutral, and the number of positive charges on the cation does not equal the number of negative charges on the anion, we use the number of positive charges as the subscript for the anion and the number of negative charges as the subscript for the cation. We will need three calcium ions to give a total charge of 6+ and two phosphate ions to give a charge of 6− so that the total charge is $(6+) + (6-) = 0$. The formula is written with parentheses to show that the PO_4^{3-} ion occurs two times in the formula unit.

$$Ca_3(PO_4)_2$$

Is the Answer Reasonable? We double-check to see that electrical neutrality is achieved for the compound. We have six positive charges from the three Ca^{2+} ions and six negative charges from the two PO_4^{3-} ions. The sum is zero and our compound is electrically neutral as required.

Practice Exercises

3.14 | Write the formula for the ionic compound formed from (a) potassium ion and acetate ion, (b) strontium ion and nitrate ion, and (c) Fe^{3+} and acetate ion. (*Hint:* See whether you remember these polyatomic ions before looking at the table.)

3.15 | Write the formula for the ionic compound formed from (a) Na^+ and CO_3^{2-} and (b) NH_4^+ and SO_4^{2-}.

Polyatomic ions are found in a large number of very important compounds. Examples include $CaSO_4$ (calcium sulfate, found in plaster of Paris or gypsum), $NaHCO_3$ (sodium bicarbonate, also called baking soda), NaOCl (sodium hypochlorite, in liquid laundry bleach), $NaNO_2$ (sodium nitrite, a meat preservative), $MgSO_4$ (magnesium sulfate, also known as Epsom salts), and $NH_4H_2PO_4$ (ammonium dihydrogen phosphate, a fertilizer).

3.5 | Nomenclature of Ionic Compounds

In conversation, chemists rarely use formulas to describe compounds. Instead, names are used. For example, you already know that water is the name for the compound having the formula H_2O and that sodium chloride is the name of NaCl.

At one time there was no uniform procedure for assigning names to compounds, and those who discovered compounds used whatever method they wished. Today, we know of more than 50 million different chemical compounds, so it is necessary to have a logical system for naming them. Chemists around the world now agree on a systematic method for naming substances that is overseen by the **IUPAC**. By using basic methods we are able to write the correct formula given the name for the many compounds we will encounter. Additionally, we will be able to take a formula and correctly name it, since up to this point we have used common names for substances. In addition, when we first name a compound in this book, we will give the IUPAC name first, followed by the common name, if there is one, in parentheses. We will subsequently use the common name.

Naming Ionic Compounds of Representative Elements

In this section we discuss the **nomenclature** (naming) of simple inorganic ionic compounds. In general, **inorganic compounds** are substances that would *not* be considered to be derived from hydrocarbons such as methane (CH_4), ethane (C_2H_6), and other carbon–hydrogen compounds. In naming ionic compounds, our goal is that we want a name that someone else could use to reconstruct the formula.

Naming ionic compounds

For ionic compounds, the name of the cation is given first, followed by the name of the anion. This is the same as the sequence in which the ions appear in the formula. If the metal in the compound forms only one cation, such as Na^+ or Ca^{2+}, the cation is specified by just giving the English name of the metal. The anion in a binary compound is formed from a nonmetal and its name is created by adding the suffix *-ide* to the stem of the name for the nonmetal. An example is KBr, potassium bromide. Table 3.6 lists some common **monatomic** (one-atom) negative ions and their names. It is also useful to know that the *-ide* suffix is usually used only for monatomic ions, with just two common exceptions—*hydroxide ion* (OH^-) and *cyanide ion* (CN^-).[2]

■ To keep the name as simple as possible, we give the minimum amount of information necessary to be able to reconstruct the formula. To write the formula of an ionic compound, we only need the formulas of the ions.

To form the name of an ionic compound, we simply specify the names of the cation and anion. We do not need to state how many cations or anions are present, since once we know what the ions are we can assemble the formula correctly just by taking them in a ratio that gives electrical neutrality.

Monatomic anion names

Table 3.6 **Monatomic Negative Ions**

H^-	Hydride	N^{3-}	Nitride	O^{2-}	Oxide	F^-	Fluoride
C^{4-}	Carbide	P^{3-}	Phosphide	S^{2-}	Sulfide	Cl^-	Chloride
Si^{4-}	Silicide	As^{3-}	Arsenide	Se^{2-}	Selenide	Br^-	Bromide
				Te^{2-}	Telluride	I^-	Iodide

Example 3.5
Naming Compounds and Writing Formulas

(a) What is the name of $SrBr_2$? (b) What is the formula for aluminum selenide?

■ **Analysis:** Both compounds are ionic, and we will name the first one using the names of the elements with the appropriate endings for the anion. For the second compound, we will write the formula using the concept of electrical neutrality.

■ **Assembling the Tools:** The tools that we will use will be the ones for naming ionic compounds and the concept that ionic compounds must be electrically neutral. In naming ionic compounds, we follow the sequence of the ions in the formula and we add the suffix *-ide* to the stem of the anion. In writing the formula for an ionic compound, we write the symbols in the order of the names and we make sure that the number of each element makes the compound electrically neutral.

■ **Solution:** (a) The compound $SrBr_2$ is composed of the elements Sr and Br. Sr is a metal from Group 2A, and Br is a nonmetal from Group 7A. Compounds of a metal and nonmetal are ionic, so we use the rules for naming ionic compounds. The cation simply takes the name of the metal, which is strontium. The anion's name is derived from bromine by replacing *-ine* with *-ide*; it is the bromide ion. The name of the compound is strontium bromide.

---

[2] If the name of a compound ends in *-ide* and it isn't either a hydroxide or a cyanide, you can feel confident the substance is a binary compound.

(b) Aluminum is a metal from Group 3A and forms the cation Al^{3+}. The *-ide* ending of selenide suggests the anion is composed of a single atom of a nonmetal. The only one that begins with the letters "selen-" is selenium, Se. (See the table inside the front cover.) The anion that is formed from selenium (Group 6A), is Se^{2-}. Since the correct formula must represent an electrically neutral formula unit, we use the number of charges on one ion as the subscript of the other—the formula is Al_2Se_3.

Are the Answers Reasonable? First, we review the analysis and check to be sure we've applied the correct rules, which we have. Next we can reverse the process to be sure our name, strontium bromide does mean $SrBr_2$, and that it is reasonable to call Al_2Se_3 aluminum selenide.

Practice Exercises

3.16 | Give the correct formulas for (a) potassium sulfide, (b) barium bromide, (c) sodium cyanide, (d) aluminum hydroxide, and (e) calcium phosphide. (*Hint:* Recall what the ending *-ide* means.)

3.17 | Give the correct names for (a) $AlCl_3$, (b) $Ba(OH)_2$, (c) NaBr, (d) CaF_2, and (e) K_3P.

Naming Cations of Transition Metals

Earlier we learned that many of the transition metals and post-transition metals are able to form more than one positive ion. Compounds that contain these different ions have different formulas, so in their names it is necessary to specify which ion is present.

The currently preferred method for naming ions of metals that can have more than one charge in compounds is called the **Stock system**. Here we use the English name followed, *without a space*, by the numerical value of the charge written as a Roman numeral in parentheses.[3] Examples using the Stock system are shown below.

■ Alfred Stock (1876–1946), a German inorganic chemist, was one of the first scientists to warn the public of the dangers of mercury poisoning.

Fe^{2+}	iron(II)	$FeCl_2$	iron(II) chloride
Fe^{3+}	iron(III)	$FeCl_3$	iron(III) chloride
Cr^{2+}	chromium(II)	CrS	chromium(II) sulfide
Cr^{3+}	chromium(III)	Cr_2S_3	chromium(III) sulfide

Remember that *the Roman numeral equals the positive charge on the metal ion*; it is not necessarily a subscript in the formula. For example, copper forms two oxides, one containing the Cu^+ ion and the other containing the Cu^{2+} ion. Their formulas are Cu_2O and CuO and their names are as follows:[4]

TOOLS

Using the Stock system

Cu^+	copper(I)	Cu_2O	copper(I) oxide
Cu^{2+}	copper(II)	CuO	copper(II) oxide

These copper compounds illustrate that in deriving the formula from the name, you must figure out the formula from the ionic charges, as previously discussed in this section and illustrated in Example 3.5.

Example 3.6
Naming Compounds and Writing Formulas

The compound $MnCl_2$ has a number of commercial uses, including as a disinfectant, in the manufacture of batteries, and for purifying natural gas. What is the name of the compound?

---

[3] Silver and nickel are almost always found in compounds as Ag^+ and Ni^{2+}, respectively. Therefore, AgCl and $NiCl_2$ are almost always called simply silver chloride and nickel chloride.

[4] For some metals, such as copper and lead, one of their ions is much more commonly found in compounds than any of their others. For example, most common copper compounds contain Cu^{2+} and most common lead compounds contain Pb^{2+}. For compounds of these metals, if the charge is not indicated by a Roman numeral, we assume the ion present has a 2+ charge. Thus, it is not unusual to find $PbCl_2$ called lead chloride or for $CuCl_2$ to be called copper chloride.

Analysis: We can see that the compound is an ionic compound since it is made up of a metal and a nonmetal, so we use the rules for naming ionic compounds.

Manganese (Mn) is a transition element, and transition elements often form more than one cation, so we apply the Stock method. We also need to determine the charge on the manganese cation. We can figure this out because the sum of the charges on the manganese and chlorine ions must equal zero, and because the only ion chlorine forms has a single negative charge.

Assembling the Tools: The tool we will use to find the charge on the metal ion is the requirement that the compound be electrically neutral. Also, because the cation is that of a transition metal, the Stock system will be the tool used to specify the charge on the cation.

Solution: The anion of chlorine (the chloride ion) is Cl^-, so a total of two negative charges are supplied by the two Cl^- ions. Therefore, for $MnCl_2$ to be electrically neutral, the Mn ion must carry two positive charges, 2+. The cation is named as manganese(II), and the name of the compound is *manganese(II) chloride*.

Is the Answer Reasonable? Performing a quick check of the arithmetic assures us we've got the correct charges on the ions. Everything appears to be okay.

Example 3.7
Naming Compounds and Writing Formulas

What is the formula for cobalt(III) fluoride?

Analysis: To answer this question, we first need to determine the charges on the two ions. Then we assemble the ions into a chemical formula being sure to achieve an electrically neutral formula unit.

Assembling the Tools: We will use the same tools as in Example 3.6.

Solution: Cobalt(III) corresponds to Co^{3+}. The fluoride ion is F^-. To obtain an electrically neutral substance, we must have three F^- ions for each Co^{3+} ion, so the formula is CoF_3.

Is the Answer Reasonable? We can check to see that we have the correct formulas of the ions and that we've combined them to achieve an electrically neutral formula unit. This will tell us we've obtained the correct answer.

Practice Exercises

3.18 | Name the compounds Li_2S, Mg_3P_2, $NiCl_2$, $TiCl_2$, and Fe_2O_3. Use the Stock system where appropriate. (*Hint:* Determine which metals can have more than one charge.)

3.19 | Write formulas for (a) aluminum sulfide, (b) strontium fluoride, (c) titanium(IV) oxide, (d) cobalt(II) oxide, and (e) gold(III) oxide.

Naming Ionic Compounds Containing Polyatomic Ions

TOOLS

Naming with polyatomic ions

■ It is important that you learn the formulas (including charges) and the names of the polyatomic ions in Table 3.5. You will encounter them frequently throughout your chemistry course.

The extension of the nomenclature system to include ionic compounds containing polyatomic ions is straightforward. Most of the polyatomic ions listed in Table 3.5 are anions and their names are used without modification as the second word in the name of the compound. For example, Na_2SO_4 contains the sulfate ion, SO_4^{2-}, and is called sodium sulfate. Similarly, $Cr(NO_3)_3$ contains the nitrate ion, NO_3^-. Chromium is a transition element, and in this compound its charge must be 3+ to balance the negative charges of three NO_3^- ions. Therefore, $Cr(NO_3)_3$ is called chromium(III) nitrate.

Among the ions in Table 3.5, the only cation that forms compounds that can be isolated is ammonium ion, NH_4^+. It forms ionic compounds such as NH_4Cl (ammonium chloride) and $(NH_4)_2SO_4$ (ammonium sulfate) even though NH_4^+ is not a metal cation. Notice that $(NH_4)_2SO_4$ is composed of two polyatomic ions.

Example 3.8
Naming Compounds and Writing Formulas

What is the name of $Mg(ClO_4)_2$, a compound used commercially for removing moisture from gases?

Analysis: To answer this question, it is essential that you recognize that the compound contains a polyatomic ion since ClO_4 is in parentheses. If you've learned the contents of Table 3.5, you know that "ClO_4" is the formula (without the charge) of the perchlorate ion. With the charge, the ion's formula is ClO_4^-. We also have to decide whether we need to apply the Stock system in naming the metal Mg.

Assembling the Tools: We will use the names of polyatomic ions in Table 3.5 and the tools about deciding whether or not to use the Stock system.

Solution: Magnesium is in Group 2A, and it only forms the ion Mg^{2+}. Therefore, we don't need to use the Stock system in naming the cation; it is named simply as "magnesium." The anion is perchlorate, so the name of $Mg(ClO_4)_2$ is *magnesium perchlorate*.

Is the Answer Reasonable? We can check to be sure we've named the anion correctly, and we have. The metal is magnesium, which only forms Mg^{2+}. Therefore, the answer seems to be correct.

Practice Exercises

3.20 | What are the names of (a) Li_2CO_3, (b) $KMnO_4$, and (c) $Fe(OH)_3$? (*Hint:* Recall the names of the polyatomic ions and the positions of Li, K, and Fe in the periodic table.)

3.21 | Write the formulas for (a) potassium chlorate, (b) sodium hypochlorite, and (c) nickel(II) phosphate.

Naming Hydrates

In Chapter 1 we discussed compounds called hydrates, such as $CuSO_4 \cdot 5H_2O$. Usually, hydrates are ionic compounds whose crystals contain water molecules in fixed proportions relative to the ionic substance. To name them, we provide two pieces of information: the name of the ionic compound and the number of water molecules in the formula. The number of water molecules is specified using the following Greek prefixes:

TOOLS
Greek prefixes

mono- = 1
di- = 2
tri- = 3
tetra- = 4
penta- = 5

hexa- = 6
hepta- = 7
octa- = 8
nona- = 9
deca- = 10

These prefixes precede the word "hydrate." Thus, $CuSO_4 \cdot 5H_2O$ is named as "copper sulfate *pentahydrate*." Similarly, $CaSO_4 \cdot 2H_2O$ is named calcium sulfate dihydrate, and $FeCl_3 \cdot 6H_2O$ is iron(III) chloride hexahydrate.[5]

---

[5] Chemical suppliers (who do not always follow current rules of nomenclature) sometimes indicate the number of water molecules using a number and a dash. For example, one supplier lists $Ca(NO_3)_2 \cdot 4H_2O$ as "Calcium nitrate, 4-hydrate."

3.6 | Molecular Compounds

The concept of molecules dates to the time of Dalton's atomic theory, where a part of his theory was that atoms of elements combine in fixed numerical ratios to form "molecules" of a compound. By our modern definition *a* **molecule** *is an electrically neutral particle consisting of two or more atoms*. Accordingly, the term molecule applies to many elements such as H_2 and O_2 as well as to compounds.

Experimental Evidence for Molecules

One phenomenon that points to the existence of molecules is called **Brownian motion**, named after Robert Brown (1773–1858), the Scottish botanist who first observed it. When very small particles such as tiny grains of pollen are suspended in a liquid and observed under a microscope, the tiny particles are seen to be constantly jumping and jiggling about. It appears as though they are continually being knocked back and forth by collisions with something. One explanation is that this "something" is *molecules* of the liquid. The microscopic particles are constantly bombarded by molecules of the liquid, but because the suspended particles are so small, the collisions are not occurring equally on all sides. The unequal numbers of collisions cause the lightweight particles to jerk about. There is additional evidence for molecules, and today scientists accept the existence of molecules as fact.

Looking more closely, within molecules the atoms are held to each other by attractions called **chemical bonds**, which are electrical in nature. In molecular compounds chemical bonds arise from the sharing of electrons between one atom and another. We will discuss such bonds at considerable length in Chapters 9 and 10. What is important to know about molecules now is that *the group of atoms that make up a molecule move about together and behave as a single particle*, just as the various parts that make up a car move about as one unit. The chemical formulas that we write to describe the compositions of molecules are called **molecular formulas,** which specify the actual numbers of atoms of each kind that make up a single molecule.

Compare the structures of water and sodium chloride in Figure 3.17. Water is a discrete unit with the two hydrogen atoms bonded to the oxygen atom. In contrast, in sodium chloride, the ions are packed as close as possible to each other; each cation has six anions next to it, and each anion has six cations next to it. It cannot be said that one sodium ion "belongs" to one chloride ion. Instead, there is an attraction between each ion and its nearest neighbors of the opposite charge.

Molecular Compounds Made from Nonmetals

■ Carbon monoxide is a poisonous gas found in the exhaust of automobiles, and we exhale carbon dioxide.

As a general rule, *molecular compounds are formed when nonmetallic elements combine*. For example, you learned that H_2 and O_2 combine to form molecules of water. Similarly, carbon and oxygen combine to form either carbon monoxide, CO, or carbon dioxide, CO_2. (Both are gases that are formed in various amounts as products in the combustion of fuels such as gasoline and charcoal.) Although molecular compounds can be formed by the direct combination of elements, often they are the products of reactions between compounds. You will encounter many such reactions in your study of chemistry.

Although there are relatively few nonmetals, the number of molecular substances formed by them is huge. This is because of the variety of ways in which nonmetals combine as well as the varying degrees of complexity of their molecules. Variety and complexity reach a maximum with compounds in which carbon is combined with a handful of other elements such as hydrogen, oxygen, and nitrogen. There are so many of these compounds, in fact, that their study encompasses the chemical specialties called **organic chemistry** and **biochemistry.**

Molecules vary in size from small to very large. Some contain as few as two atoms (diatomic molecules). Most molecules are more complex, however, and contain more

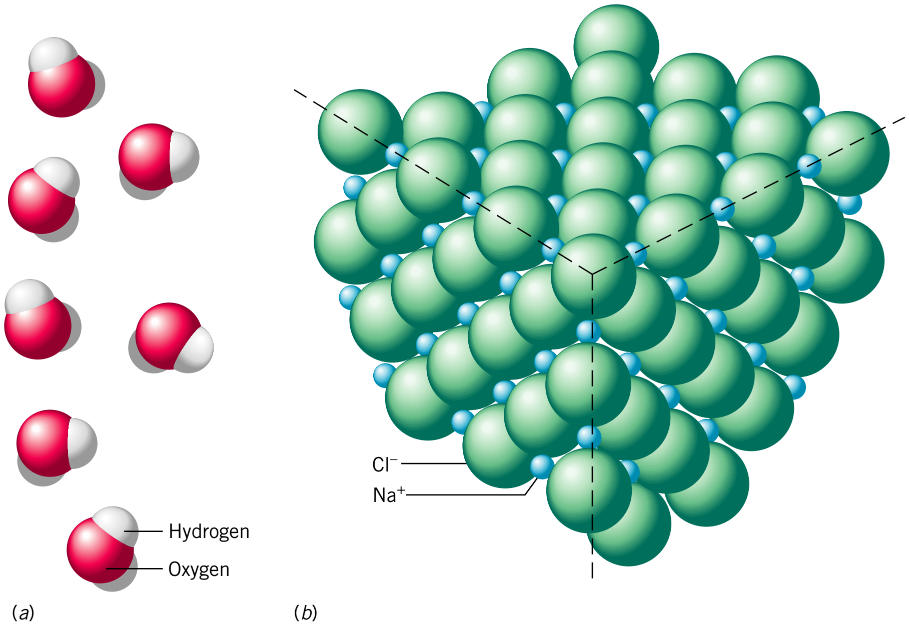


Figure 3.17 | **Molecular and ionic substances.** *(a)* In water there are discrete molecules that each consist of one atom of oxygen and two atoms of hydrogen. Each particle has the formula H_2O. *(b)* In sodium chloride, ions are packed in the most efficient way. Each Na^+ is surrounded by six Cl^-, and each Cl^- is surrounded by six Na^+. Because individual molecules do not exist, we simply specify the ratio of ions as NaCl.

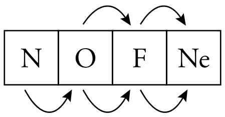
atoms. Molecules of water (H_2O), for example, have three atoms and those of ordinary table sugar ($C_{12}H_{22}O_{11}$) have 45. There also are molecules that are very large, such as those that occur in plastics and in living organisms, some of which contain millions of atoms.

At this early stage we can only begin to look for signs of order among the vast number of nonmetal–nonmetal compounds. To give you a taste of the subject, we will look briefly at some simple compounds that the nonmetals form with hydrogen, as well as some simple compounds of carbon.

Hydrogen-containing Compounds

Hydrogen forms a variety of compounds with other elements, and the formulas of the simple hydrogen compounds of the nonmetals (called **nonmetal hydrides**) are given in Table 3.7.[6] These compounds provide an opportunity to observe how we can use the periodic table as an aid in remembering factual information, in this case, the formulas of the hydrogen compounds of the nonmetals. Notice that the number of hydrogen atoms combined with the nonmetal atom equals *the number of spaces to the right that we have to move in the periodic table to get to a noble gas.* (You will learn *why* this is so in Chapter 9, but for now we can just use the periodic table to help us remember the formulas.)

Two steps, so oxygen
combines with two hydrogens to give H_2O.



Three steps, so nitrogen
combines with three hydrogens to give NH_3.

TOOLS

Predicting formulas of nonmetal hydrogen compounds

Also note in Table 3.7 that the formulas of the hydrogen compounds within a given group of the periodic table are similar for nonmetals. If you know the formula for the hydrogen compound of the top member of the group, then you know the formulas of all of them in that group.

---

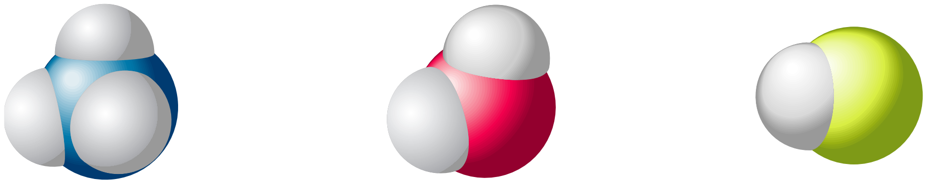
[6] Table 3.7 shows how the formulas are normally written. The order in which the hydrogens appear in the formula is not of concern to us now. Instead, we are interested in the *number* of hydrogens that combine with a given nonmetal.

Table 3.7 Simple Hydrogen Compounds of the Nonmetallic Elements

	Group			
Period	**4A**	**5A**	**6A**	**7A**
2	CH_4	NH_3	H_2O	HF
3	SiH_4	PH_3	H_2S	HCl
4	GeH_4	AsH_3	H_2Se	HBr
5		SbH_3	H_2Te	HI

■ Many of the nonmetals form more complex compounds with hydrogen, but we will not discuss them here.

We live in a three-dimensional world, and this is reflected in the three-dimensional shapes of molecules. The shapes of the simple nonmetal hydrogen containing compounds of nitrogen, oxygen, and fluorine are illustrated as space-filling models in Figure 3.18. The geometric shapes of molecules will be described futher in Chapter 10.



Ammonia, NH_3 Water, H_2O Hydrogen fluoride, HF

Figure 3.18 | **Nonmetal hydrides of nitrogen, oxygen, and fluorine.**

Carbon Compounds: The Basis of Organic Chemistry

■ Our goal at this time is to acquaint you with some of the important kinds of organic compounds we encounter regularly, so our discussion here is brief.

Among all the elements, carbon is unique in the variety of compounds it forms with elements such as hydrogen, oxygen, and nitrogen, and their study constitutes the major specialty, organic chemistry. The term "organic" here comes from an early belief that these compounds could only be made by living organisms. We now know this isn't true, but the name organic chemistry persists nonetheless.

Organic compounds are around us everywhere and we will frequently use such substances as examples in our discussions. Therefore, it will be helpful if you can begin to learn some of them now.

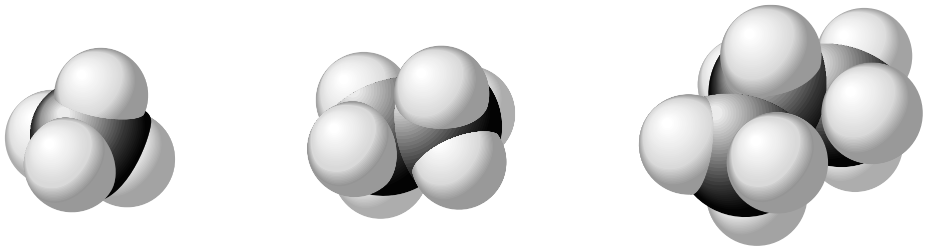
The study of organic chemistry begins with **hydrocarbons** (compounds of hydrogen and carbon). The simplest hydrocarbon is methane, CH_4, which is a member of a series of hydrocarbons with the general formula C_nH_{2n+2}, where n is an integer (i.e., a whole number). The first six members of this series, called the **alkane** series, are listed in Table 3.8 along with their boiling points. Notice that as the molecules become larger, their boiling points increase. Molecules of methane, ethane, and propane are illustrated as space-filling models in Figure 3.19.

The alkanes are common substances. They are the principal constituents of petroleum from which most of our useful fuels are produced. Methane itself is the major component of natural gas that is often used for home heating and cooking. Gas-fired barbecues and

Table 3.8 Hydrocarbons Belonging to the Alkane Series

Compound	**Name**	**Boiling Point (°C)**	**Structural Formula**
CH_4	Methane[a]	−161.5	CH_4
C_2H_6	Ethane[a]	−88.6	CH_3CH_3
C_3H_8	Propane[a]	−42.1	$CH_3CH_2CH_3$
C_4H_{10}	Butane[a]	−0.5	$CH_3CH_2CH_2CH_3$
C_5H_{12}	Pentane	36.1	$CH_3CH_2CH_2CH_2CH_3$
C_6H_{14}	Hexane	68.7	$CH_3CH_2CH_2CH_2CH_2CH_3$

[a] Gases at room temperature (25 °C) and atmospheric pressure.



Methane, CH_4 Ethane, C_2H_6 Propane, C_3H_8

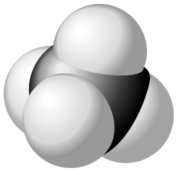
Figure 3.19 | **The first three members of the alkane series of hydrocarbons.**

some homes use propane as a fuel, and butane is the fuel in inexpensive cigarette lighters.[7] Hydrocarbons with higher boiling points are found in gasoline, kerosene, paint thinners, diesel fuel, and even candle wax.

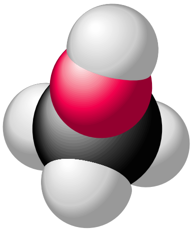
Alkanes are not the only class of hydrocarbons. For example, there are three two-carbon hydrocarbons. In addition to ethane, C_2H_6, there are ethene (ethylene), C_2H_4, which has two fewer hydrogens in the molecule than ethane, and ethyne (acetylene), C_2H_2 (which is the fuel used in *acetylene* welding torches).

The hydrocarbons serve as the foundation for organic chemistry. Derived from them are various other classes of organic compounds. An example is the class of compounds called **alcohols**, in which the atoms OH replace a hydrogen in the hydrocarbon. Thus, *methanol*, CH_3OH (also called *methyl alcohol*), is related to methane, CH_4, by removing one H and replacing it with OH (Figure 3.20). Methanol is used as a fuel and as a raw material for making other organic chemicals. Another familiar alcohol is *ethanol* (also called *ethyl alcohol*), C_2H_5OH. Ethanol, known as grain alcohol because it is obtained from the fermentation of grains, is in alcoholic beverages. It is also mixed with gasoline to reduce petroleum consumption. A 10% ethanol/90% gasoline mixture is known as gasohol, and an 85% mixture of ethanol and gasoline is called E85.

■ Methanol is also known as wood alcohol because it was originally made by distilling wood. It is quite poisonous. Ethanol in high doses is also a poison.



Methane



Methanol

Figure 3.20 | **Relationship between an alkane and an alcohol.** The alcohol methanol is derived from methane by replacing one H by OH.

Alcohols constitute just one class of compound derived from hydrocarbons. We will discuss some others after you've learned more about how atoms bond to each other and about the structures of molecules.

Writing Formulas for Organic Compounds

Organic formulas can be written in different ways, depending on what information is needed. A molecular formula such as C_2H_6 for ethane or C_3H_8 for propane simply indicates the number of each type of atom in the molecule. The order of the elements in the molecular formula starts with carbon since it is the basis for organic compounds. This is followed by hydrogen, and then the rest of the elements are written in alphabetical order. For example, sucrose is $C_{12}H_{22}O_{11}$. There are exceptions; for example, if we wish to emphasize an alcohol, the OH is separated and listed last, as in ethanol, C_2H_5OH. Condensed structural formulas indicate how the carbon atoms are connected. Ethane is written as CH_3CH_3, and propane is $CH_3CH_2CH_3$ in the condensed structural formula format.

Practice Exercises

3.22 | Gasoline used in modern cars is a complex mixture of hundreds of different organic compounds. Less than 1% of gasoline is actually octane. Write the formula for octane using the molecular and condensed structural formats. (*Hint:* To figure out the number of carbon atoms, recall the meaning of the Greek prefix "octa.")

3.23 | What is the formula of the alkane hydrocarbon having 10 carbon atoms, decane? Write both the molecular formula and the condensed structural formula.

3.24 | On the basis of the discussions in this section, what are the formulas of (a) propanol and (b) butanol? Write both the molecular formula and the condensed structural formula.

---

[7] Propane and butane are gases when they're at the pressure of the air around us, but become liquids when compressed. When you purchase these substances, they are liquids with pressurized gas above them. The gas can be drawn off and used by opening a valve to the container.

3.7 | Nomenclature of Molecular Compounds

Binary Molecular Compounds

Just as in naming the ionic compound, we want to be able to translate a chemical formula into a name that anyone with a background in chemistry can understand. For a binary molecular compound, therefore, we must indicate which two elements are present and the number of atoms of each in a molecule of the substance.

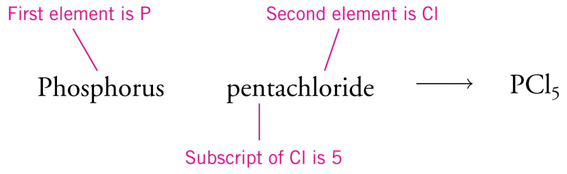
To identify the first element in a formula, we just specify its English name. Thus, for HCl the first word in the name is "hydrogen" and for PCl_5 the first word is "phosphorus." To identify the second element, we append the suffix *-ide* to the stem of the element's English name just as we did for the monoatomic anions in ionic compounds.

To form the name of the compound, we place the two parts of the name one after another. Therefore, the name of HCl is hydrogen chloride. However, to name PCl_5, we need a way to specify the number of Cl atoms bound to the phosphorus in the molecule. This is done using the Greek prefixes listed in the hydrates section on page 89; the main difference is that the prefix mono- is often omitted.

To name PCl_5, therefore, we add the prefix penta- to chloride to give the name phosphorus pentachloride. Notice how easily this allows us to translate the name back into the formula.

TOOLS

Naming binary molecular compounds



The prefix mono- is used when we want to emphasize that only one atom of a particular element is present. For instance, carbon forms two compounds with oxygen, CO and CO_2. To clearly distinguish between them, the first is called carbon monoxide (one of the "o"s is omitted to make the name easier to pronounce) and the second is carbon dioxide.

As indicated above, the prefix mono- is often omitted from a name. Therefore, in general, if there is no prefix before the name of an element, we take it to mean there is only one atom of that element in the molecule. An exception to this is in the names of binary compounds of nonmetals with hydrogen. An example is hydrogen sulfide. The name tells us the compound contains the two elements hydrogen and sulfur. We don't have to be told how many hydrogens are in the molecule because, as you learned earlier, we can use the periodic table to determine the number of hydrogen atoms in molecules of the simple nonmetal, hydrogen-containing compounds. Sulfur is in Group 6A, so to get to the noble gas column (Group 8A) we have to move two steps to the right; the number of hydrogens combined with the atom of sulfur is two. The formula for hydrogen sulfide is therefore H_2S.

Example 3.9

Naming Compounds and Writing Formulas

(a) What is the name of $AsCl_3$? (b) What is the formula for dinitrogen tetraoxide?

■ **Analysis:** (a) In naming compounds, the first step is to determine the type of compound involved. Looking at the periodic table, we see that $AsCl_3$ is made up of two nonmetals, so we conclude that it is a molecular compound.

(b) To write the formula from the name, we convert the prefixes to numbers.

■ Now that we've discussed both ionic and molecular compounds, this first step in the analysis will be particularly important, because different rules apply depending on the type of compound being named.

■ **Assembling the Tools:** (a) We apply the tool for naming molecular compounds from the molecule's formula described previously.

(b) The meanings of the Greek prefixes will be our tool to convert the prefixes to numbers that we apply as subscripts for the chemical symbols in the formula.

Solution: (a) In $AsCl_3$, As is the symbol for arsenic and Cl is the symbol for chlorine. The first word in the name is just arsenic and the second will contain chloride with an appropriate prefix to indicate number. There are three Cl atoms, so the prefix is tri. Therefore, the name of the compound is *arsenic trichloride*.

(b) As we did earlier for phosphorus pentachloride, we convert the prefixes to numbers and apply them as subscripts.

$$\overset{\text{First element is N.}}{\underset{\text{Subscript of N is 2.}}{\text{dinitrogen}}} \qquad \overset{\text{Second element is O.}}{\underset{\text{Subscript of O is 4.}}{\text{tetraoxide}}} \longrightarrow N_2O_4$$

Sometimes we drop the *a* before an *o* for ease of pronunciation. N_2O_4 would then be named dinitrogen tetroxide.

Are the Answers Reasonable? To feel comfortable with the answers, be sure to double-check for careless errors. Next, take your answers and reverse the process. Does arsenic trichloride result in the original formula, $AsCl_3$? Does N_2O_4 have the name of dinitrogen tetraoxide? We can say yes to both and have confidence in our work.

Practice Exercises

3.25 | Name the following compounds using Greek prefixes when needed: (a) PCl_3, (b) SO_2, (c) Cl_2O_7, and (d) H_2S. (*Hint:* See the list of prefixes above.)

3.26 | Write formulas for the following compounds: (a) arsenic pentachloride, (b) sulfur hexachloride, (c) disulfur dichloride, and (d) hydrogen telluride.

Common Names for Molecular Compounds

Not every compound is named according to the systematic procedure we have described so far. Many familiar substances were discovered long before a systematic method for naming them had been developed, and they acquired common names that are so well known that no attempt has been made to rename them. For example, following the scheme described above we might expect that H_2O would have the name hydrogen oxide (or even dihydrogen monoxide). Although this isn't wrong, the common name water is so well known that it is always used. Another example is ammonia, NH_3, whose odor you have no doubt experienced while using household ammonia solutions or the glass cleaner Windex®. Common names are used for the other hydrogen-containing compounds of the nonmetals in Group 5A as well. The compound PH_3 is called phosphine and AsH_3 is called arsine.

Common names are also used for very complex substances. An example is sucrose, which is the chemical name for table sugar, $C_{12}H_{22}O_{11}$. The structure of this compound is pretty complex, and its name assigned following the systematic method is equally complex. It is much easier to say the simple name sucrose, and be understood, than to struggle with the cumbersome systematic name for this common compound.

Naming Molecular and Ionic Compounds

In this chapter we've discussed how to name two classes of compounds, molecular and ionic, and you saw that slightly different rules apply to each. To name chemical compounds successfully we need to make a series of decisions based on the rules we just covered. We can summarize this decision process in a flow chart such as the one shown in Figure 3.21. The next example illustrates how to use the flow chart, and when working on the Review Questions, you may want to refer to Figure 3.21 until you are able to develop the skills that will enable you to work without it.

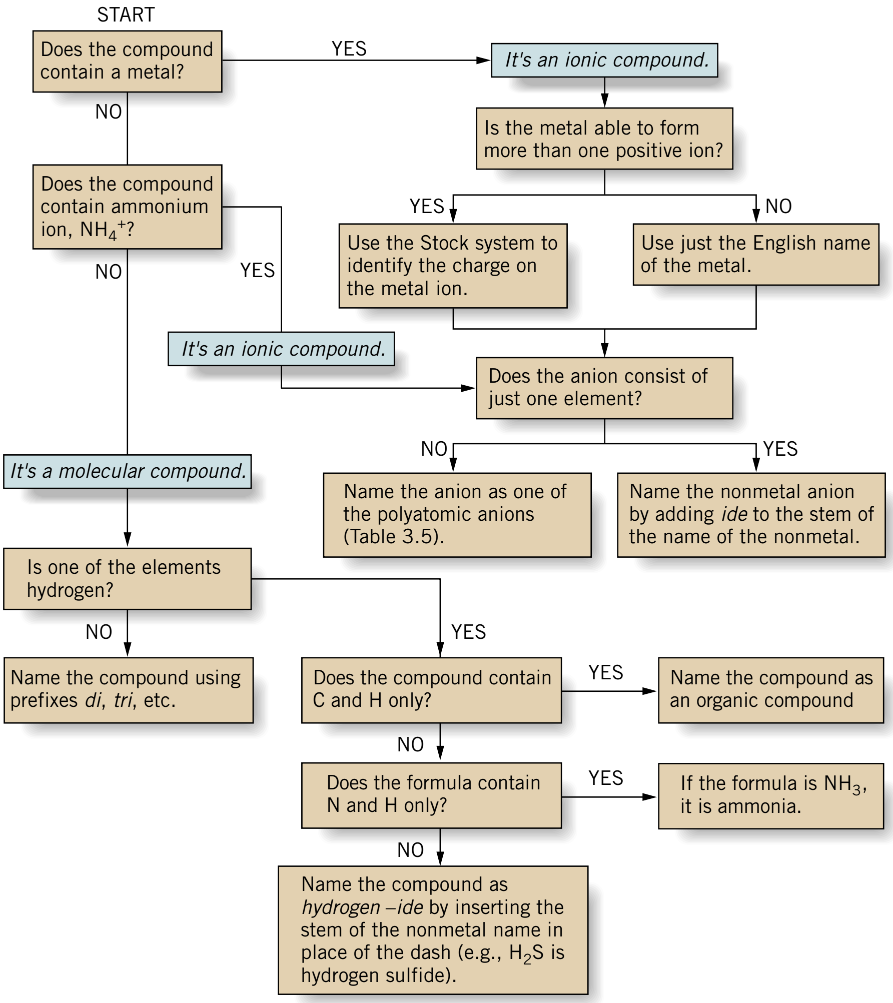

START
Does the compound contain a metal?
YES
It's an ionic compound.
Is the metal able to form more than one positive ion?
YES
Use the Stock system to identify the charge on the metal ion.
NO
Use just the English name of the metal.
NO
Does the compound contain ammonium ion, NH_4^+?
YES
It's an ionic compound.
Does the anion consist of just one element?
NO
Name the anion as one of the polyatomic anions (Table 3.5).
YES
Name the nonmetal anion by adding *ide* to the stem of the name of the nonmetal.
NO
It's a molecular compound.
Is one of the elements hydrogen?
NO
Name the compound using prefixes *di*, *tri*, etc.
YES
Does the compound contain C and H only?
YES
Name the compound as an organic compound
NO
Does the formula contain N and H only?
YES
If the formula is NH_3, it is ammonia.
NO
Name the compound as *hydrogen –ide* by inserting the stem of the nonmetal name in place of the dash (e.g., H_2S is hydrogen sulfide).

Figure 3.21 | **Flowchart for naming molecular and ionic compounds.**

Example 3.10
Applying the Rules for Naming Compounds

What is the name of (a) $CrCl_3$, (b) P_4S_3, and (c) NH_4NO_3?

■ **Analysis:** We need to start by determining whether or not the compounds are ionic or molecular, and then follow the rules given for naming the appropriate type of compound.

■ **Assembling the Tools:** For each compound, we use the tools summarized in Figure 3.21 and proceed through the decision processes to arrive at the name of the compound.

■ **Solution:** (a) Starting at the top of Figure 3.21, we first determine that the compound contains a metal (Cr), so it's an ionic compound. Next, we see that the metal is a transition element, and chromium is one of those that forms more than one cation, so we have to apply the Stock method. To do this, we need to know the charge on the metal ion. We can figure this out using the charge on the anion and the fact that the compound must be electrically neutral overall. The anion is formed from chlorine, so its charge is 1− (the anion is Cl^-). Since there are three chlorine ions, the metal ion must be Cr^{3+}; we name the metal *chromium(III)*. Next, we see that there is only one nonmetallic element in the compound, Cl, so the name of the anion ends in -ide; it's the *chloride* ion. The compound $CrCl_3$ is therefore named *chromium(III) chloride*.

(b) Once again, we start at the top of Figure 3.21. First, we determine that the compound doesn't contain a metal or NH_4^+, so the compound is molecular. It doesn't contain hydrogen, so we are led to the decision that we must use Greek prefixes to specify the numbers of atoms of each element. Applying the procedure on page 94, the name of the compound P_4S_3 is *tetraphosphorus trisulfide*.

(c) We begin at the top of Figure 3.21. Studying the formula, we see that it does not contain the symbol for a metal, so we proceed down the left side of the figure. The formula does contain NH_4^+, which indicates that the compound contains the *ammonium* ion, NH_4^+ (it's an ionic compound). The rest of the formula is NO_3, which consists of more than one atom. This suggests the polyatomic anion, NO_3^- (*nitrate* ion). The name of the compound NH_4NO_3 is *ammonium nitrate*.

■ **Are the Answers Reasonable?** To check the answers in a problem of this kind, review the decision processes that led you to the names. In Part (a), you can check to be sure you've calculated the charge on the chromium ion correctly. Also, check to be sure you've used the correct names of any polyatomic ions. Doing these things will show that you've named the compounds correctly.

Practice Exercises

3.27 | The compound I_2O_5 is used in respirators where it serves to react with highly toxic carbon monoxide to give the much less toxic gas, carbon dioxide. What is the name of I_2O_5? (*Hint:* Is this a molecular or an ionic compound?)

3.28 | The compound $Cr(C_2H_3O_2)_3$ is used in the tanning of leather. What is the name for this compound?

3.29 | The compound $KClO_4$ is used in fireworks. What is the name for this compound?

Summary

Atomic Structure. Atoms can be split into **subatomic particles,** such as **electrons**, **protons**, and **neutrons**. **Nucleons** are particles that make up the atomic **nucleus** and include the protons, each of which carries one unit of **positive charge** (charge = 1+) and the neutrons that have no charge. The number of protons is called the **atomic number** *(Z)* of the element. Each element has a different atomic number. The electrons, each with one unit of **negative charge** (charge = 1−), are found outside the nucleus; their number equals the atomic number in a neutral atom. Isotopes of an element have identical atomic numbers but different numbers of neutrons. In more modern terms, an **element** can be defined as a substance whose atoms all have the same number of protons in their nuclei.

Atomic Mass. An element's **atomic mass** (**atomic weight**) is the relative mass of its atoms on a scale in which atoms of carbon-12 have a mass of exactly 12 u (**atomic mass units**). Most elements occur in nature as uniform mixtures of a small number of **isotopes,** whose masses differ slightly. However, all isotopes of an element have very nearly identical chemical properties, and the percentages of the isotopes that make up an element are generally so constant throughout the world that we can say that the average mass of their atoms is a constant.

The Periodic Table. In the modern **periodic table** the elements are arranged in rows, called **periods**, in order of increasing atomic number. The rows are stacked so that elements in the columns, called **groups** or **families**, have similar chemical and physical properties. The A-group elements (IUPAC Groups 1, 2, and 13–18) are called **representative elements**; the B-group elements (IUPAC Groups 3–12) are called **transition elements.** The two long rows of **inner transition elements** located below the main body of the table consist of the **lanthanides**, which follow La ($Z = 57$), and the **actinides,** which follow Ac ($Z = 89$). Certain groups are given family names: Group 1A (Group 1), except for hydrogen, are the **alkali metals** (the alkalis); Group 2A (Group 2) are the **alkaline earth metals**; Group 7A (Group 17) are the **halogens**; and Group 8A (Group 18) are the **noble gases**.

Metals, Nonmetals, and Metalloids. Most elements are **metals**; they occupy the lower left-hand region of the periodic table (to the left of a line drawn approximately from boron, B, to astatine, At). **Nonmetals** are found in the upper right-hand region of the table. **Metalloids** occupy a narrow band between the metals and nonmetals.

Metals exhibit a **metallic luster,** tend to be **ductile** and **malleable**, and conduct heat and electricity. Nonmetals tend to be brittle, lack metallic luster, and are nonconductors of electricity. Many nonmetals are gases. **Metalloids** have properties intermediate between those of metals and nonmetals and are **semiconductors** of electricity.

Ions and Ionic Compounds. **Binary ionic** compounds are formed when metals react with nonmetals. In the reaction, electrons are transferred from a metal to a nonmetal. The metal atom becomes a positive ion (a **cation**); the nonmetal atom becomes a negative ion (an **anion**). The formula of an ionic compound specifies the smallest whole-number ratio of the ions. The smallest unit of an ionic compound is called a **formula unit,** which specifies the smallest whole-number ratio of the ions that produces electrical neutrality. Many ionic compounds also contain **polyatomic ions**—ions that are composed of two or more atoms.

Naming Ionic Compounds. In naming an ionic compound, the cation is specified first, followed by the anion. Metal cations take the English name of the element, and when more than one positive ion can be formed by the metal, the **Stock system** is used to identify the amount of positive charge on the cation. This is done by placing a Roman numeral equal to the positive charge in parentheses following the name of the metal. Simple **monatomic** anions are formed by nonmetals, and their names are formed by adding the suffix -ide to the stem of the nonmetal's name. Only two common polyatomic anions (cyanide and hydroxide) end in the suffix -ide.

Molecules and Molecular Compounds. **Molecules** are electrically neutral particles consisting of two or more atoms. The erratic movements of microscopic particles suspended in a liquid (**Brownian motion**) can be interpreted as the result of collisions with molecules of the liquid. Molecules are held together by **chemical bonds** that arise from the sharing of electrons between atoms. The formulas we write for molecules are **molecular formulas**. Molecular compounds are formed when nonmetals combine with each other. The simple **nonmetal hydrides** have formulas that can be remembered by the position of the nonmetal in the periodic table. **Organic compounds** are **hydrocarbons,** or compounds considered to be derived from hydrocarbons by replacing H atoms with other atoms.

Properties of Molecular and Ionic Compounds. We found that it is often possible to distinguish ionic compounds from molecular compounds by their ability to **conduct electricity**. Molecular compounds are generally poor electrical conductors, whereas ionic compounds when melted into the liquid state or dissolved in water will conduct electricity readily.

Naming Molecular Compounds. The system of **nomenclature** for **binary** molecular **inorganic compounds** uses a set of **Greek prefixes** to specify the numbers of atoms of each kind in the formula of the compound. The first element in the formula is specified by its English name; the second element takes the suffix -ide, which is added to the stem of the English name. For simple nonmetal hydrogen compounds, it is not necessary to specify the number of hydrogens in the formula. Many familiar substances, as well as very complex molecules, are usually identified by **common names**. The decision tree in Figure 3.21 is a helpful tool in naming ionic and molecular compounds.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Number of subatomic particles in atoms (page 68)

There are three important relationships between the numbers of **protons, neutrons (the nucleons),** and **electrons.** These relationships are:

$$\text{Number of electrons} = \text{number of protons}$$
$$\text{Atomic number } (Z) = \text{number of protons}$$
$$\text{Mass number } (A) = \text{number of protons} + \text{number of neutrons}$$

Atomic symbols for isotopes (page 68)

The mass number (*A*) comes before the element symbol as a superscript and the atomic number (*Z*) also comes before the element as a subscript.

$${}^{A}_{Z}X$$

Relative atomic masses (page 70)

Atomic masses are relative to the mass of a ^{12}C atom that has a mass of exactly 12 atomic mass units (u). Therefore, the atomic mass of ^{12}C is exactly 12 u.

Periodic table (page 73)

The periodic table has several tool icons in this chapter illustrating its use in a variety of different ways. For example, we can obtain atomic numbers and average masses of the elements from the periodic table. The periodic table lists the atoms by atomic number and organizes them by their properties in periods and groups. We can also tell if a element is a metal, nonmetal, or metalloid from it position in the periodic table (page 75).

Properties of metals (page 76)
Metals have specific properties such as luster, electrical and heat conductivity, malleability, and ductility, which help distinguish them from nonmetals and metalloids.

Ionic compounds (page 80)
The rules permit us to write correct chemical formulas for ionic compounds. You will need to learn to use the periodic table to remember the charges on the cations and anions of the representative metals and nonmetals.

Predicting cation charge (page 81)
For the metals in Groups 1A and 2A, we can use the elements' positions in the periodic table to obtain the charges on their ions.

Predicting anion charge (page 81)
From a nonmetal's position in the periodic table, we can determine the charge of the monatomic anions.

Formulas for ionic compounds (page 82)
Following the rules gives us the correct formulas for ionic compounds with electrically neutral formula units and with subscripts in the smallest set of whole numbers.

Polyatomic ions (page 84)
Certain groups of atoms arrange themselves into stable, electrically charged particles that we call polyatomic ions. It is very important that you commit to memory the names, formulas, and charges of these ions which are listed in Table 3.5. You will need them to write formulas and name compounds.

Naming ionic compounds (page 86)
These rules give us a systematic method for naming ionic compounds. The name of the cation is combined with the name of a monatomic anion. These rules are used with slight modification for cations that can have more than one possible charge (see the **Stock system**) and for situations in which a polyatomic ion is involved (see naming with **polyatomic ions**).

Monatomic anion names (page 86)
The list on this page gives the common names of anions that must be remembered so you can use them to name ionic compounds.

Using the Stock system (page 87)
The Stock system specifies the charge of a cation by placing a Roman numeral in parentheses just after the name of the cation. The Stock system and its Roman numerals are only used for cations that can have more than one possible charge.

Naming with polyatomic ions (page 88)
Naming compounds that contain polyatomic anions is done by specifying the cation name, using the Stock system if needed, and then specifying the polyatomic anion name as given in Table 3.5. The one polyatomic cation, the ammonium ion (NH_4^+), uses its name and then the appropriate name of the anion.

Greek prefixes (page 89)
This page has a list of the Greek prefixes from one to ten that you should know for naming molecular compounds and hydrates.

Predicting formulas of nonmetal hydrogen compounds (page 91)
From a nonmetal's position in the periodic table we can write the formula of its simple hydrogen compound. These are given in Table 3.7.

Naming binary molecular compounds (page 94)
These rules give us a logical system for naming binary molecular compounds by specifying the number of each type of atom using Greek prefixes.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Atomic Masses and Atomic Structure

3.1 What are the names, symbols, and electrical charges of the three subatomic particles introduced in this chapter?

3.2 Where in an atom is nearly all of its mass concentrated? Explain your answer in terms of the particles that contribute to this mass.

3.3 What is a *nucleon*? Which ones have we studied?

3.4 How was the charge-to-mass ratio of the electron determined?

3.5 How did Robert Millikan determine the charge of an electron, and how did this allow the mass of the electron to be determined?

3.6 How was the proton discovered?

3.7 What experiment did Rutherford carry out to determine the existence of the nucleus?

3.8 Define the terms *atomic number* and *mass number.* What symbols are used to designate these terms?

3.9 Consider the symbol $^{a}_{b}X$, where X stands for the chemical symbol for an element. What information is given in locations **(a)** *a* and **(b)** *b*?

3.10 Write the symbols of the isotopes that contain the following. (Use the table of atomic masses and numbers printed inside the front cover for additional information, as needed.)

(a) An isotope of iodine whose atoms have 78 neutrons

(b) An isotope of strontium whose atoms have 52 neutrons

(c) An isotope of cesium whose atoms have 82 neutrons

(d) An isotope of fluorine whose atoms have 9 neutrons

3.11 What is wrong with the following statement? "The atomic mass of an atom of chlorine is 35.453 u."

The Periodic Table

3.12 In the compounds formed by Li, Na, K, Rb, and Cs with chlorine, how many atoms of Cl are there per atom of each metal? In the compounds formed by Be, Mg, Ca, Sr, and Ba with chlorine, how many atoms of Cl are there per atom of each metal? How did this kind of information lead Mendeleev to develop his periodic table?

3.13 On what basis did Mendeleev construct his periodic table? On what basis are the elements arranged in the modern periodic table?

3.14 On the basis of their positions in the periodic table, why is it not surprising that strontium-90, a dangerous radioactive isotope of strontium, replaces calcium in newly formed bones?

3.15 In the refining of copper, sizable amounts of silver and gold are recovered. Why is this not surprising?

3.16 Why would you reasonably expect cadmium to be a contaminant in zinc but not in silver?

3.17 Using the symbol for nitrogen, $^{14}_{7}\mathrm{N}^{0}_{2}$, indicate what information is conveyed by the two superscripts, and what information is conveyed by the two subscripts.

3.18 Make a rough sketch of the periodic table and mark off those areas where you would find **(a)** the representative elements, **(b)** the transition elements, and **(c)** the inner transition elements.

3.19 Which of the following is

(a) an alkali metal? Ca, Cu, In, Li, S

(b) a halogen? Ce, Hg, Si, O, I

(c) a transition element? Pb, W, Ca, Cs, P

(d) a noble gas? Xe, Se, H, Sr, Zr

(e) a lanthanide element? Th, Sm, Ba, F, Sb

(f) an actinide element? Ho, Mn, Pu, At, Na

(g) an alkaline earth metal? Mg, Fe, K, Cl, Ni

Metals, Nonmetals, and Metalloids

3.20 Name five physical properties that we usually observe for metals.

3.21 Why is mercury used in thermometers? Why is tungsten used in lightbulbs?

3.22 Which nonmetals occur as monatomic gases (i.e., gases whose particles consist of single atoms)?

3.23 Which two elements exist as liquids at room temperature and pressure?

3.24 Which physical property of metalloids distinguishes them from metals and nonmetals?

3.25 Sketch the shape of the periodic table and mark off those areas where we find **(a)** metals, **(b)** nonmetals, and **(c)** metalloids.

3.26 Most periodic tables have a heavy line that looks like a staircase starting from boron down to polonium. What information does this line convey?

3.27 Which metals can you think of that are commonly used to make jewelry? Why isn't iron used to make jewelry? Why isn't potassium used?

3.28 What trends—regular changes in physical or chemical properties—in the periodic table have been mentioned in this chapter?

3.29 Find a periodic table on the Internet that lists physical properties of the elements. Can you distinguish trends in the periodic table based on **(a)** melting point, **(b)** boiling point, or **(c)** density?

Ionic Compounds

3.30 Describe what kind of event must occur (involving electrons) if the atoms of two different elements are to react to form an ionic compound.

3.31 With what kind of elements do metals react?

3.32 What is an ion? How does it differ from an atom or a molecule?

3.33 Why do we use the term *formula unit* for ionic compounds instead of the term *molecule*?

3.34 Consider the sodium atom and the sodium ion.

(a) Write the chemical symbol of each.

(b) Do these particles have the same number of nuclei?

(c) Do they have the same number of protons?

(d) Could they have different numbers of neutrons?

(e) Do they have the same number of electrons?

3.35 Define *cation, anion*, and *polyatomic ion.*

3.36 How many electrons has a titanium atom lost if it has formed the ion Ti^{4+}? What are the total numbers of protons and electrons in a Ti^{4+} ion?

3.37 If an atom gains an electron to become an ion, what kind of electrical charge does the ion have?

3.38 How many electrons has a nitrogen atom gained if it has formed the ion N^{3-}? How many protons and electrons are in an N^{3-} ion?

3.39 What is wrong with the formula $RbCl_3$? What is wrong with the formula SNa_2?

3.40 A student wrote the formula for an ionic compound of titanium as Ti_2O_4. What is wrong with this formula? What should the formula be?

3.41 What are the formulas of the ions formed by **(a)** iron, **(b)** cobalt, **(c)** mercury, **(d)** chromium, **(e)** tin, and **(f)** manganese?

3.42 Which of the following formulas are incorrect? Write the formulas for the compounds correctly. **(a)** NaO_2, **(b)** RbCl, **(c)** K_2S, **(d)** Al_2Cl_3, **(e)** MgP_2

3.43 What are the formulas (including charges) for **(a)** cyanide ion, **(b)** ammonium ion, **(c)** nitrate ion, **(d)** sulfite ion, **(e)** chlorate ion, and **(f)** sulfate ion?

3.44 What are the formulas (including charges) for **(a)** hypochlorite ion, **(b)** bisulfate ion, **(c)** phosphate ion, **(d)** dihydrogen phosphate ion, **(e)** permanganate ion, and **(f)** oxalate ion?

3.45 What are the names of the following ions? **(a)** $Cr_2O_7^{2-}$, **(b)** OH^-, **(c)** $C_2H_3O_2^-$, **(d)** CO_3^{2-}, **(e)** CN^-, **(f)** ClO_4^-

3.46 Write correct balanced equations for the reactions between **(a)** calcium and chlorine, **(b)** magnesium and oxygen, **(c)** aluminum and oxygen, and **(d)** sodium and sulfur.

3.47 Write the balanced equations for the following reactions:

(a) Iron(III) hydroxide reacts with hydrogen chloride forming water and iron(III) chloride.

(b) Silver nitrate is reacted with barium chloride to form silver chloride and barium nitrate.

3.48 Write the balanced equations for the following reactions:

(a) Propane reacts with oxygen to form carbon dioxide and water.

(b) Sodium metal is added to water and the products are sodium hydroxide and hydrogen gas.

Molecular Compounds

3.49 With what kind of elements do nonmetals react?

3.50 Which are the only elements that exist as free, individual atoms when not chemically combined with other elements?

3.51 Write chemical formulas for the elements that normally exist in nature as diatomic molecules.

3.52 Which kind of elements normally combine to form molecular compounds?

3.53 Why are nonmetals found in more compounds than are metals, even though there are fewer nonmetals than metals?

3.54 Most compounds of aluminum are ionic, but a few are molecular. How do we know that Al_2Cl_6 is molecular?

3.55 Without referring to Table 3.7 but using the periodic table, write chemical formulas for the simplest hydrogen compounds of **(a)** carbon, **(b)** nitrogen, **(c)** tellurium, and **(d)** iodine.

3.56 The simplest hydrogen compound of phosphorus is phosphine, a highly flammable and poisonous compound with an odor of decaying fish. What is the formula for phosphine?

3.57 Astatine, a member of the halogen family, forms a compound with hydrogen. Predict its chemical formula.

3.58 Under appropriate conditions, tin can be made to form a simple molecular compound with hydrogen. Predict its formula.

3.59 Write the chemical formulas for **(a)** methane, **(b)** ethane, **(c)** propane, and **(d)** butane. Give one practical use for each of these hydrocarbons.

3.60 What are the formulas for **(a)** methanol and **(b)** ethanol?

3.61 What is the formula for the alkane, decane, that has 10 carbon atoms?

3.62 Candle wax is a mixture of hydrocarbons, one of which is an alkane with 23 carbon atoms. What is the formula for this hydrocarbon?

3.63 The formula for a compound is correctly given as $C_6H_{12}O_6$. State two reasons why we expect this to be a molecular compound, rather than an ionic compound.

3.64 Explore the Internet and find a reliable source of structures for molecular compounds. For Problems 3.59 to 3.63, print out the ball-and-stick and space-filling models of the compounds mentioned.

Nomenclature of Ionic and Molecular Compounds

3.65 What is the difference between a binary compound and one that is diatomic? Give examples that illustrate this difference.

3.66 In naming the compounds discussed in this chapter, why is it important to know whether a compound is molecular or ionic?

3.67 In naming ionic compounds of the transition elements, why is it essential to give the charge on the anion?

3.68 Describe **(a)** the three situations in which Greek prefixes are used and **(b)** when Roman numerals are used.

Review Problems

Atomic Masses and Isotopes

3.69 The chemical substance in natural gas is a compound called methane. Its molecules are composed of carbon and hydrogen, and each molecule contains four atoms of hydrogen and one atom of carbon. In this compound, 0.33597 g of hydrogen is combined with 1.0000 g of carbon-12. Use this information to calculate the atomic mass of the element hydrogen.

3.70 Carbon tetrachloride contains one carbon and four chlorine atoms. For this compound 11.818 g of chlorine combine with 1.000 g of C-12. Using this information, calculate the atomic mass of chlorine.

OH **3.71** A certain element *X* forms a compound with oxygen in which there are two atoms of *X* for every three atoms of O. In this compound, 1.125 g of *X* are combined with 1.000 g of oxygen. Use the average atomic mass of oxygen to calculate the average atomic mass of *X*. Use your calculated atomic mass to identify the element *X*.

3.72 Nitrogen reacts with a metal to form a compound in which there are three atoms of the metal for each atom of nitrogen. If 1.486 g of the metal reacts with 1.000 g of nitrogen, what is the calculated atomic mass of the metal? Use your calculated atomic mass to identify the metal.

3.73 If an atom of carbon-12 had been assigned a relative mass of 24.0000 u, what would be the average atomic mass of hydrogen relative to this mass?

3.74 One atom of ^{109}Ag has a mass that is 9.0754 times that of a ^{12}C atom. What is the atomic mass of this isotope of silver expressed in atomic mass units?

Atomic Structure

ILW **3.75** Naturally occurring copper is composed of 69.17% of ^{63}Cu, with an atomic mass of 62.9396 u, and 30.83% of ^{65}Cu, with an atomic mass of 64.9278 u. Use these data to calculate the average atomic mass of copper.

3.76 Naturally occurring magnesium (one of the elements in milk of magnesia) is composed of 78.99% of ^{24}Mg (atomic mass = 23.9850 u), 10.00% of ^{25}Mg (atomic mass = 24.9858 u), and 11.01% of ^{26}Mg (atomic mass = 25.9826 u). Use these data to calculate the average atomic mass of magnesium.

ILW **3.77** Give the numbers of neutrons, protons, and electrons in the atoms of each of the following isotopes. **(a)** radium-226, **(b)** ^{206}Pb, **(c)** carbon-14, **(d)** ^{23}Na (Use the table of atomic masses and numbers printed inside the front cover for additional information, as needed.)

3.78 Give the numbers of electrons, protons, and neutrons in the atoms of each of the following isotopes. **(a)** cesium-137, **(b)** ^{238}U, **(c)** iodine-131, **(d)** ^{285}Cn (As necessary, consult the table of atomic masses and numbers printed inside the front cover.)

3.79 Iodine-131 is used to treat overactive thyroids; it has a mass of 130.9061 u. Give the number of protons, neutrons, and electrons in the atom.

3.80 In the polyatomic ion TcO_4^-, Tc has a hypothetical charge of 7+. The ^{99}Tc isotope is used in medicine for imaging purposes. It has a mass of 98.90625 u. Give the number of protons, neutrons, and electrons for a Tc^{7+} ion.

Ionic Compounds

3.81 Use the periodic table, but not Table 3.3, to write the symbols for the ions of **(a)** K, **(b)** Br, **(c)** Mg, **(d)** S, and **(e)** Al.

3.82 Use the periodic table, but not Table 3.3, to write the symbols for ions of **(a)** barium, **(b)** oxygen, **(c)** fluorine, **(d)** strontium, and **(e)** rubidium.

OH **3.83** Write formulas for ionic compounds formed between **(a)** Na and Br, **(b)** K and I, **(c)** Ba and O, **(d)** Mg and Br, and **(e)** Ba and F.

3.84 Write the formulas for the ionic compounds formed by the following transition metals with the chloride ion, Cl^-: **(a)** chromium, **(b)** iron, **(c)** manganese, **(d)** copper, and **(e)** zinc.

3.85 Write formulas for the ionic compounds formed from **(a)** K^+ and nitrate ion, **(b)** Ca^{2+} and acetate ion, **(c)** ammonium ion and Cl^-, **(d)** Fe^{3+} and carbonate ion, and **(e)** Mg^{2+} and phosphate ion.

3.86 Write formulas for the ionic compounds formed from **(a)** Zn^{2+} and hydroxide ion, **(b)** Ag^+ and chromate ion, **(c)** Ba^{2+} and sulfite ion, **(d)** Rb^+ and sulfate ion, and **(e)** Li^+ and bicarbonate ion.

3.87 Each of the following metals can form two compounds with oxygen. Write their formulas. **(a)** lead, **(b)** tin, **(c)** manganese, **(d)** iron, and **(e)** copper.

3.88 Write formulas for the ionic compounds formed from Cl^- and **(a)** cadmium ion, **(b)** silver ion, **(c)** zinc ion, and **(d)** nickel ion.

Nomenclature

3.89 Name the following ionic compounds: **(a)** CaS, **(b)** $AlBr_3$, **(c)** Na_3P, **(d)** Ba_3As_2, **(e)** Rb_2S.

3.90 Name the following ionic compounds: **(a)** NaF, **(b)** Mg_2C, **(c)** Li_3N, **(d)** Al_2O_3, **(e)** K_2Se.

3.91 Name the following molecular compounds: **(a)** SiO_2, **(b)** XeF_4, **(c)** P_4O_{10}, **(d)** Cl_2O_7.

3.92 Name the following molecular compounds: **(a)** ClF_3, **(b)** S_2Cl_2, **(c)** N_2O_5, **(d)** $AsCl_5$.

3.93 Name the following ionic compounds using the Stock system: **(a)** FeS, **(b)** CuO, **(c)** SnO_2, **(d)** $CoCl_2 \cdot 6H_2O$.

3.94 Name the following ionic compounds using the Stock system: **(a)** Mn_2O_3, **(b)** Hg_2Cl_2, **(c)** PbS, **(d)** $CrCl_3 \cdot 4H_2O$.

3.95 Name the following. If necessary, refer to Table 3.5 on page 84. **(a)** $NaNO_2$, **(b)** $KMnO_4$, **(c)** $MgSO_4 \cdot 7H_2O$, **(d)** $KSCN$

3.96 Name the following. If necessary, refer to Table 3.5 on page page 84. **(a)** K_3PO_4, **(b)** $NH_4C_2H_3O_2$, **(c)** $Fe_2(CO_3)_3$, **(d)** $Na_2S_2O_3 \cdot 5H_2O$

3.97 Identify each of the following as molecular or ionic and give its name:

(a) $CrCl_2$
(b) S_2Cl_2
(c) $NH_4C_2H_3O_2$
(d) SO_3
(e) KIO_3
(f) P_4O_6
(g) $CaSO_3$
(h) $AgCN$
(i) $ZnBr_2$
(j) H_2Se

3.98 Identify each of the following as molecular or ionic and give its name:

(a) $V(NO_3)_3$
(b) $Co(C_2H_3O_2)_2$
(c) Au_2S_3
(d) Au_2S
(e) $GeBr_4$
(f) K_2CrO_4
(g) $Fe(OH)_2$
(h) I_2O_4
(i) I_4O_9
(j) P_4Se_3

OH **3.99** Write formulas for the following.

(a) sodium monohydrogen phosphate
(b) lithium selenide
(c) chromium(III) acetate
(d) disulfur decafluoride
(e) nickel(II) cyanide
(f) iron(III) oxide
(g) antimony pentafluoride

3.100 Write formulas for the following.

(a) dialuminum hexachloride
(b) tetraarsenic decaoxide
(c) magnesium hydroxide
(d) copper(II) bisulfate
(e) ammonium thiocyanate
(f) potassium thiosulfate
(g) diiodine pentaoxide

3.101 Write formulas for the following.

(a) ammonium sulfide
(b) chromium(III) sulfate hexahydrate
(c) silicon tetrafluoride
(d) molybdenum(IV) sulfide
(e) tin(IV) chloride
(f) hydrogen selenide
(g) tetraphosphorus heptasulfide

3.102 Write formulas for the following.

(a) mercury(II) acetate
(b) barium hydrogen sulfite
(c) boron trichloride
(d) calcium phosphide
(e) magnesium dihydrogen phosphate
(f) calcium oxalate
(g) xenon tetrafluoride

3.103 The compounds Se_2S_6 and Se_2S_4 have been shown to be antidandruff agents. What are their names?

3.104 The compound P_2S_5 is used to manufacture safety matches. What is the name of this compound?

Additional Exercises

3.105 An element has 24 protons in its nucleus.

- **(a)** Is the element a metal, a nonmetal, or a metalloid?
- **(b)** On the basis of the average atomic mass, write the symbol for the element's most abundant isotope.
- **(c)** How many neutrons are in the isotope you described in part (b)?
- **(d)** How many electrons are in atoms of this element?
- **(e)** How many times heavier than ^{12}C is the average atom of this element?

3.106 The elements in Group 1A and Group 7A of the periodic table are some of the most reactive elements. What is the difference in reactivity between these two groups?

3.107 Iron is composed of four isotopes with the percentage abundances and atomic masses given in the following table. Calculate the average atomic mass of iron.

Isotope	Percentage Abundance	Atomic Mass (u)
^{54}Fe	5.80	53.9396
^{56}Fe	91.72	55.9349
^{57}Fe	2.20	56.9354
^{58}Fe	0.28	57.9333

OH ***3.108** Bromine (shown in Figure 3.13, page 77) is a dark red liquid that vaporizes easily and is very corrosive to the skin. It is used commercially as a bleach for fibers and silk. Naturally occurring bromine is composed of two isotopes: ^{79}Br, with a mass of 78.9183 u, and ^{81}Br, with a mass of 80.9163 u. Use this information and the average atomic mass of bromine given in the table on the inside front cover of the book to calculate the percentage abundances of these two isotopes.

3.109 One atomic mass unit has a mass of $1.6605402 \times 10^{-24}$ g. Calculate the mass, in grams, of one "average" atom of magnesium. What is the mass of one "average" atom of iron, expressed in grams? Use these two answers to determine how many atoms of Mg are in 24.305 g of magnesium and how many atoms of Fe are in 55.847 g of iron. Compare your answers. What conclusions can you draw from the results of these calculations? Without actually performing any calculations, how many atoms do you think would be in 40.078 g of calcium?

OH **3.110** What are the formulas for mercury(I) nitrate dihydrate and mercury(II) nitrate monohydrate?

3.111 Consider the following substances: Cl_2, CaO, HBr, $CuCl_2$, AsH_3, $NaNO_3$, and NO_2.

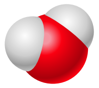
- **(a)** Which are binary substances?
- **(b)** Which is a triatomic molecule?
- **(c)** In which do we find only electron sharing?
- **(d)** Which are diatomic?
- **(e)** In which do we find only attractions between ions?
- **(f)** Which are molecular?
- **(g)** Which are ionic?

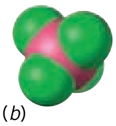
OH **3.112** Write the balanced chemical equation for the reaction between elements with atomic numbers of **(a)** 20 and 35, **(b)** 6 and 17, **(c)** 13 and 16. For each of these, determine the ratio of the mass of the heavier element to the lighter element in the compound.

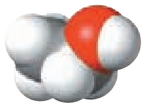
3.113 Write the balanced gas phase chemical equation for the reaction of dinitrogen pentoxide with sulfur dioxide to form sulfur trioxide and nitrogen oxide. What small, whole-number ratios are expected for oxygen in the nitrogen oxides and the sulfur oxides?

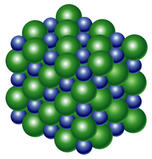
3.114 Bromine is a diatomic molecule, and it has two isotopes, ^{79}Br and ^{81}Br, with a natural abundance of about 50% for each isotope. How many different molecules can be formed for Br_2? What instrument would you use to distinguish between the different molecules?

3.115 Using the figures below, match the image with the correct molecular formula: CH_3CH_2OH, NaCl, $SnCl_4$, and H_2O. Write the names of the compounds.

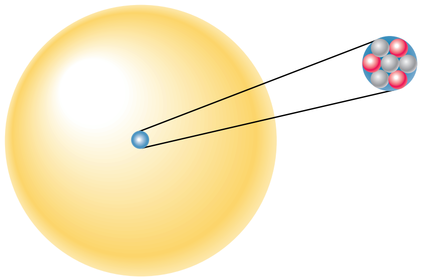

(*a*)


(*b*)


(*c*)


(*d*)

3.116 What color are the protons, neutrons, and electrons in the following figure? What element is it? What is the mass number of the atom? Write the symbol for the atom using the ${}^{a}_{b}X$ notation.



Exercises in Critical Thinking

3.117 Imagine a world where, for some reason, hydrogen and helium have not been discovered. Would Mendeleev have had enough information to predict their existence?

3.118 Around 1750 Benjamin Franklin knew of two opposite types of electric charge, produced by rubbing a glass rod or amber rod with fur. He decided that the charge developed on the glass rod should be the "positive" charge, and from there on charges were defined. What would have changed if Franklin had decided the amber rod was the positive charge?

3.119 Explore the Internet and find a reliable source of physical properties of elements and compounds. Justify how you decided the site was reliable.

3.120 Spreadsheet applications such as Microsoft Excel can display data in a variety of ways, some of which are shown throughout this book. What method of displaying periodic trends (for example, line graphs, tables, bar graphs, 3-D views, etc.) is most effective for your learning style? Explain your answer by stating why your chosen display is better than the others.

3.121 Scientists often validate measurements, such as measuring the circumference of the earth, by using two independent methods to measure the same value. Describe two independent methods for determining the atomic mass of an element. Explain how these methods are truly independent.

3.122 Immediately after the Big Bang, helium and other very light elements were formed. Later, more elements were formed up to about magnesium. It was not until stars were formed that heavier atoms up to iron were created. The heaviest naturally occurring elements did not form until the explosion of massive stars in supernovas. Look at the periodic table and divide it up by these masses. Is there any trend or information about these elements that you can determine from this information?

3.123 Sir James Chadwick discovered the neutron. The Web site for the Nobel Prize committee contains his acceptance speech for the Nobel Prize he won in physics in 1935. Read the speech and draw a diagram that summarizes the experiment.

4 The Mole and Stoichiometry

Chapter Outline

4.1 | The Molecular Scale versus the Laboratory Scale

4.2 | Chemical Formulas and Stoichiometry

4.3 | Determining Empirical and Molecular Formulas

4.4 | The Mole and Chemical Reactions

4.5 | Limiting Reactants

4.6 | Theoretical Yield and Percentage Yield

Billions of hamburgers are served each year in restaurants and fast-food establishments. Typically the hamburger will have one beef patty, one sliced bun, several pickles, and a tablespoon of sauce. At the start, restaurants order their food supplies by the pound. In preparing an order for 1,000 hamburgers, the purchasing agent needs to know that one hamburger requires 1/4 pound of beef, there are about 200 pickle slices in a pound, a tablespoon of ketchup weighs 0.25 ounces, and each hamburger bun weighs 1.5 ounces. From this information the purchasing agent can order 250 pounds of ground beef, 5 pounds of pickles, 16 pounds of ketchup, and 95 pounds of hamburger buns. Instead of counting out individual items, the agent converts them to the mass that is required. This chapter illustrates that chemists count their atoms and molecules the same way, by weighing them. Figure 4.1 illustrates the difference between making a single hamburger and 1,000 hamburgers. © Michael Sofronski/The Image Works

This Chapter in Context

In this chapter we use the tools from Chapters 2 and 3 to learn the fundamentals of chemical calculations called **stoichiometry** (stoy-kee-AH-meh-tree), which loosely translates as “the measure of the elements.” You will find that these calculations are very important for success in the chemistry laboratory. You will also find this chapter to be important for future courses in organic chemistry, biochemistry, and almost any other advanced laboratory course in the sciences.

Stoichiometry involves converting chemical formulas and equations that represent individual atoms, molecules, and formula units to the laboratory scale that uses milligrams, grams, and even kilograms of these substances. To do this we introduce the concept of the *mole.* The mole allows the chemist to scale up from the atomic/molecular level to the laboratory scale much as the purchasing agent in Figure 4.1 scales up the amount of ingredients from a single hamburger to a mass-production scale. Our stoichiometric calculations are usually conversions from one set of units to another using dimensional analysis. To be successful using dimensional analysis calculations we need two things: a knowledge of the equalities that can be made into conversion factors and a logical sequence of steps to guide us from the starting set of units to the desired units. Figure 4.6, at the end of this chapter, is a flowchart that organizes the sequence of conversion steps and the conversion factors used in stoichiometric calculations in this chapter. In the following chapters, as we learn new concepts, they will be added to this flowchart to illustrate how many of our chemical ideas are interrelated.

4.1 | The Molecular Scale versus the Laboratory Scale

We can tell from the fundamental measurements of the mass of the proton, neutron, and electron in Chapter 3 that even the largest of the atoms must have extremely small masses and correspondingly small sizes. Consequently, any sample of matter that is observable by the naked eye must have very large numbers of atoms or molecules. The methods of calculation developed in Chapter 2, along with the mole concept, allow us to count by weighing and then use that information to solve some very interesting problems.

Counting by weighing is familiar to everyone even if we are not aware of it. Our introductory example of mass-produced hamburgers illustrated one use of counting by weighing.

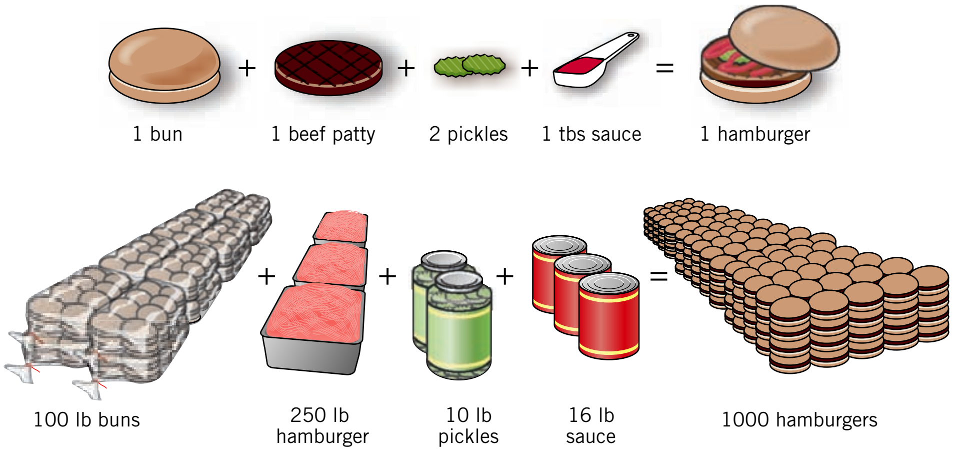


Figure 4.1 | **Hamburgers on the small and large scale.** Making a single hamburger requires one bun, one hamburger patty, two pickles, and a tablespoon of sauce. To make a thousand hamburgers we need 100 lb of rolls, 250 lb of hamburger meat, 10 lb of pickles, and 16 lb of sauce.

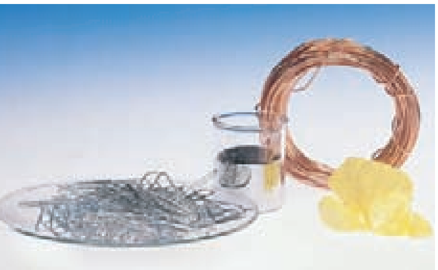


Figure 4.2 | **Moles of elements.** Each sample of these elements—iron, mercury, copper, and sulfur—contains the same number of atoms. *(Michael Watson)*

A pound of chocolate chips counts out the needed number of chocolate chips for your cookies. A quarter pound of rice counts out the correct number of rice grains to accompany a family meal. Weighing a bag of dimes, knowing that each dime weighs 2.27 grams, will allow you to calculate the number of coins. Similarly, the mass of a chemical substance can be used to determine the number of atoms or molecules in the sample. This last conversion is possible because of the mole concept.

Defining the Mole

In Chapter 2 we noted that the mole is the SI unit for the amount of substance. The amount of substance does not refer to the mass or volume of your sample but it does refer to the number of atoms, molecules, or formula units, etc. in your sample. Exactly **one mole (mol) is defined as a number equal to the number of atoms in exactly 12 grams of ^{12}C atoms.** Based on this definition and the fact that the average atomic masses in the periodic table are relative values, we can deduce that we will have a mole of atoms of any element if we weigh an amount equal to the atomic mass in gram units (this is often called the gram atomic mass).

TOOLS

Atomic mass

$$1 \text{ mole of element } X = \text{gram atomic mass of } X$$

For example, the atomic mass of sulfur is 32.06 u and one mole of sulfur will weigh 32.06 g and it will have as many atoms as exactly 12 g of carbon-12. Figure 4.2 is a photo showing one mole of some common elements—iron, mercury, copper, and sulfur.

- Mole is a Latin word with several meanings, including a shapeless mass, a large number, or trouble or difficulty.

The Mole Concept Applied to Compounds

- Many chemists still use terms like molecular weight and atomic weight for molecular mass and atomic mass.

Molecules and ionic compounds discussed in Chapter 3 have definite formulas. For molecular compounds and elements, adding the atomic masses of all atoms in the formula results in the **molecular mass** (sometimes called the **molecular weight**). The gram molecular mass of a molecular substance (the mass in grams equal to the molecular mass) is also equal to one mole of those molecules.

TOOLS

Molecular mass or formula mass

$$1 \text{ mole of molecule } X = \text{gram molecular mass of } X$$

For example, the molecular mass of water is 18.02 u, the sum of the atomic masses of two H atoms and one O atom. Similarly, the gram **formula mass** of an ionic compound is the sum of the atomic masses of all the atoms in the formula of an ionic compound expressed with units of grams.

$$1 \text{ mole of ionic compound } X = \text{gram formula mass of } X$$

The ionic compound Al_2O_3 has two aluminum atoms with an atomic mass of 26.98 u each and three oxygen atoms with a mass of 16.00 u each. This adds up to 101.96 u, and one mole of Al_2O_3 has a gram formula mass of 101.96 g.

There is a distinct similarity between all three equations above. To simplify discussions we will often use the following relationship between moles and mass unless one of the other, equivalent, definitions provides more clarity.

TOOLS

Molar mass

$$1 \text{ mole of } X = \text{gram molar mass of } X$$

The gram molar mass (often shortened to **molar mass**) is simply the mass of the substance under consideration without distinguishing whether the substance is an element, a molecule, or an ionic compound. Figure 4.3 depicts one mole of four different compounds.

Figure 4.3 | **Moles of compounds.** One mole of four different compounds: water, sodium chloride, copper sulfate pentahydrate, and sodium chromate. Each sample contains the same number of formula units or molecules. *(Michael Watson)*

Converting between Mass and Moles

At this point we recognize the above relationships or equalities as the necessary information for conversion problems similar to those in Chapter 2. Now, however, the problems will be couched in chemical terms.

Example 4.1

Converting from Grams to Moles

Titanium(IV) oxide is one of the best sunscreens because it completely blocks ultraviolet radiation from reaching the skin. In an experiment to prepare TiO_2, we start with a 23.5 g sample of titanium. How many moles of Ti do we have?

■ **Analysis:** We see that the problem starts with a certain mass of titanium and asks us to convert it to moles. This uses the tool we just described that equates moles and grams of an element.

■ **Assembling the Tools:** We have a tool for converting the mass into moles that states 1 mol *X* is equal to the atomic mass of *X* with gram units. Now we make it specific for titanium by replacing *X* with the symbol for titanium and entering the atomic mass of Ti to get

$$1\text{ mol Ti} = 47.867\text{ g Ti}$$

(When we work problems that include tabulated data, such as the atomic mass of Ti, we will always *keep at least one more significant figure* than the given information.)

■ **Solution:** Start by setting up the problem in the form of an equation showing the number and its units that we start with and the units we want when we're finished.

$$\underset{\text{start}}{23.5\text{ g Ti}} = ?\ \underset{\text{end}}{\text{mol Ti}}$$

■ Solving stoichiometry problems is much like giving directions from your house to your college. You need both the starting and ending points. Stating the problem as an equation gives you these reference points, and the conversion factors get us from the start to the end.

Now use the equality between mass and moles to set up the ratio that will cancel the grams of titanium as shown below

$$23.5\ \cancel{\text{g Ti}} \times \left(\frac{1\text{ mol Ti}}{47.867\ \cancel{\text{g Ti}}}\right) = 0.491\text{ mol Ti}$$

■ **Is the Answer Reasonable?** First, be sure that the units cancel properly. Second, round all numbers to one or two significant figures and calculate an estimated answer. One way to round the numbers gives us 25/50, and that is equal to 1/2. Our answer is not very different (very different would be a factor of 10 or more) from 1/2, so our answer is reasonable.

Example 4.2
Converting from Moles to Grams

We need 0.254 moles of $FeCl_3$ for a certain experiment. How many grams do we need to weigh?

■ **Analysis:** As in the last problem the conversion is between moles and mass, but now we also need an additional step to calculate the molar mass of $FeCl_3$.

■ **Assembling the Tools:** We need the tool for calculating the molar mass of $FeCl_3$. That is the sum of masses of one mole of iron atoms and three moles of chlorine atoms.

$$\text{Molar mass FeCl}_3 = 55.845\text{ g/mol} + (3 \times 35.453\text{ g/mol}) = 162.204\text{ g/mol}$$

Now the tool that represents the equality between mass and moles can be written as

$$1\text{ mol FeCl}_3 = 162.204\text{ g FeCl}_3$$

■ **Solution:** The problem is set up by translating the question into equation form:

$$0.254\text{ mol FeCl}_3 = ?\text{ g FeCl}_3$$

Then we construct the conversion factor from the equality between mass and moles to perform the conversion:

$$0.254\ \cancel{\text{mol FeCl}_3} \times \left(\frac{162.204\text{ g FeCl}_3}{1\ \cancel{\text{mol FeCl}_3}}\right) = 41.2\text{ g FeCl}_3$$

■ **Is the Answer Reasonable?** First, we verify that the units cancel properly. Next we do an approximate calculation. If we round 0.254 to 0.25 and 162.204 to 160, the arithmetic becomes $0.25 \times 160 = 40$, which gives a result that is very close to the calculated value. Alternately we can round to one significant figure, which gives $0.3 \times 200 = 60$ and still conclude that the answer is reasonable. Remember that this is just an estimate, but it tells us that our more precise answer, 41.2 g $FeCl_3$, is in the right ballpark.

Practice Exercises

4.1 | How many moles of aluminum are there in a 3.47 gram sheet of aluminum foil used to wrap your sandwich for lunch today? (*Hint:* Recall the tool that relates the mass of an element to moles of that element.)

4.2 | Your laboratory balance can weigh samples to three decimal places. If the uncertainty in your weighing is ±0.002 g, what is the uncertainty expressed in terms of moles, if the sample being weighed is pure potassium sulfate?

Avogadro's Number

The SI definition of the mole refers to a number equal to the number of atoms in exactly 12 g of ^{12}C. Just what is that number? After much experimentation the scientific community agrees that the value, to four significant figures, is 6.022×10^{23}. This value has been named **Avogadro's number**. Now we can write a very important relationship between the atomic scale and the laboratory scale as

■ Avogadro's number was named for Amedeo Avogadro (1776–1876), an Italian chemist who was one of the pioneers of stoichiometry.

TOOLS
Avogadro's number

$$1\text{ mole of }X = 6.022 \times 10^{23}\text{ units of }X$$

The units of our chemicals can be atoms, molecules, formula units, and so on. This means that one mole of xenon atoms is the same as 6.022×10^{23} atoms of Xe. Similarly, 6.022×10^{23} molecules of NO_2 represents one mole of nitrogen dioxide molecules.

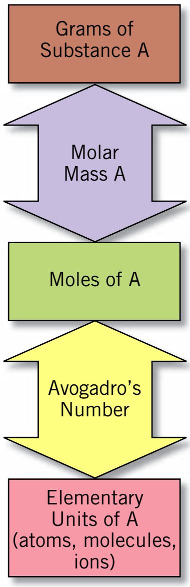
Using Avogadro's Number

The relationships developed above allow us to connect the laboratory scale with the atomic scale using our standard dimensional analysis calculations as shown in the next two examples.

Avogadro's number is the link between the moles of a substance and its elementary units. If a problem is on the laboratory scale (atoms or molecules are not mentioned) then Avogadro's number is not needed in the calculation.

Example 4.3

Converting from the Laboratory Scale to the Atomic Scale



General sequence of calculations to convert between mass and elementary units of a substance. Arrows indicate which tools apply to each conversion.

Tungsten wire is the filament inside most incandescent lightbulbs. In a typical lightbulb, the tungsten filament weighs 0.635 grams. How many atoms of tungsten are there in such a lightbulb filament?

Analysis: Let's first translate the question into an equation:

$$0.635 \text{ g tungsten} = ? \text{ atoms tungsten}$$

Here we do not have any tool that directly relates grams of tungsten to atoms of tungsten. However, we can start with the grams of tungsten and make the following *sequence of conversions.*

$$\text{grams tungsten} \longrightarrow \text{moles tungsten} \longrightarrow \text{atoms tungsten}$$

Assembling the Tools: The first tool we need is the mass-to-moles tool,

$$183.84 \text{ g W} = 1 \text{ mol W}$$

which lets us construct conversion factors between grams of tungsten and moles of tungsten. Next we need the tool for Avogadro's number that allows us to construct conversion factors between the moles of tungsten atoms and the number of tungsten atoms,

$$1 \text{ mol W} = 6.022 \times 10^{23} \text{ atoms W}$$

Solution: Having expressed the question as an equation, we can use it along with the two tools for the conversions to construct the two conversion factors. The first is

$$\frac{1 \text{ mol W}}{183.84 \text{ g W}}$$

and the second conversion factor is

$$\frac{6.022 \times 10^{23} \text{ atoms W}}{1 \text{ mol W}}$$

We multiply the original 0.635 grams of tungsten by the conversion factors to get

$$0.635 \cancel{\text{g W}} \times \left(\frac{1 \cancel{\text{mol W}}}{183.84 \cancel{\text{g W}}}\right) \times \left(\frac{6.022 \times 10^{23} \text{ atoms W}}{1 \cancel{\text{mol W}}}\right)$$
$$= 2.08 \times 10^{21} \text{ atoms W}$$

Is the Answer Reasonable? The most important check in this type of question involves the magnitude of the numbers. We know that even the smallest measurable sample of a chemical must contain a very large number of atoms. Our answer is a very large number, and therefore the answer seems reasonable.

Review Table 2.4 to see that positive exponents indicate large numbers and negative exponents indicate small numbers.

Example 4.4
Calculating the Mass of a Molecule

Carbon tetrachloride was used as a dry-cleaning fluid until it was found to be carcinogenic. What is the average mass of one molecule of carbon tetrachloride?[1]

Analysis: First, we can set up the question as an equation:

$$1 \text{ molecule carbon tetrachloride} = ? \text{ g carbon tetrachloride}$$

We can see that this problem has many steps that need to be combined to obtain the complete solution. First, we need to identify the chemical formula from its name; then we need to use that formula to calculate the molar mass of the compound. Finally, we need to construct the appropriate conversion factors to first convert one molecule to moles and then convert those moles into the mass of the carbon tetrachloride molecule.

Assembling the Tools: We first use the nomenclature tools in Chapter 3 to determine that the formula for carbon tetrachloride is CCl_4. Next, we need the tool that uses Avogadro's number,

$$6.022 \times 10^{23} \text{ molecules } CCl_4 = 1 \text{ mol } CCl_4$$

After that we need the tool to calculate the molar mass of CCl_4 as the sum of the masses of one mole of carbon and four moles of chlorine atoms, 153.823 g/mol. The molar mass is used as our tool to express the equality

$$1 \text{ mol } CCl_4 = 153.823 \text{ g } CCl_4$$

Solution: We now follow the sequence of calculations in our analysis, and will do the calculation in two steps. First, we construct a conversion factor using Avogadro's number and use it to calculate the moles of CCl_4.

$$1 \ \cancel{\text{molecule } CCl_4} \times \left(\frac{1 \text{ mol } CCl_4}{6.022 \times 10^{23} \ \cancel{\text{molecules } CCl_4}}\right) = 1.661 \times 10^{-24} \text{ mol } CCl_4$$

A second conversion factor is made from the molar mass equality to convert mol CCl_4 to g CCl_4.

$$1.661 \times 10^{-24} \ \cancel{\text{mol } CCl_4} \times \left(\frac{153.823 \text{ g } CCl_4}{1 \ \cancel{\text{mol } CCl_4}}\right) = 2.555 \times 10^{-22} \text{ g } CCl_4$$

One molecule can be considered to be an exact number. The result is that the number of significant figures to keep in the answer depends upon the number of significant figures taken from the tabulated data. Four significant figures were used for Avogadro's number and four significant figures were kept in the answer.

Is the Answer Reasonable? We expect that a single molecule, even a very large molecule, would have a very small mass. Since our answer is very small, it seems reasonable.

Practice Exercises

4.3 | Most chemistry laboratories have balances that can weigh to the nearest milligram. Would it be possible to weigh 5.64×10^{18} molecules of octadecane, $C_{18}H_{38}$, on such a balance?

4.4 | If the uncertainty in weighing a sample in the lab is ±0.002 grams, what is this uncertainty expressed in terms of molecules of sucrose, $C_{12}H_{22}O_{11}$?

---

[1] Since atomic masses given in the periodic table are weighted averages of naturally occurring isotopes, we cannot determine the exact mass of a molecule unless we know the isotope of each atom. We can, however, calculate an average mass as requested in this question.

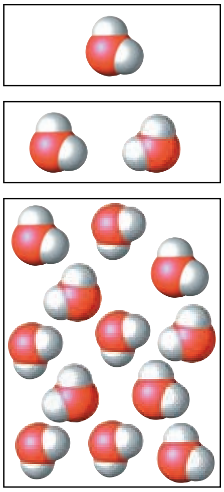
4.2 | Chemical Formulas and Stoichiometry

Mole-to-Mole Conversion Factors

The mole ratio concept that we develop here is a very powerful and important chemical tool. It allows the chemist to start with the amount of one substance and then find the chemically equivalent amount of another substance without doing the actual experiments. The relationships implied by the chemical formula allow this to happen.

Consider the chemical formula for water, H_2O:

- One molecule of water contains 2 H atoms and 1 O atom.
- Two molecules of water contain 4 H atoms and 2 O atoms.
- A dozen molecules of water contain 2 dozen H atoms and 1 dozen O atoms.
- A mole of molecules of water contains 2 moles of H atoms and 1 mole of O atoms.



Whether we're dealing with atoms, dozens of atoms, or moles of atoms, the chemical formula tells us that the ratio of H atoms to O atoms is always 2 to 1. In addition, we can write the following equivalencies concerning water molecules and moles of water molecules:

One water molecule	**One mole of water molecules**
1 molecule $H_2O \Leftrightarrow$ 2 atoms H	1 mol $H_2O \Leftrightarrow$ 2 mol H
1 molecule $H_2O \Leftrightarrow$ 1 atom O	1 mol $H_2O \Leftrightarrow$ 1 mol O
1 atom O $\Leftrightarrow$ 2 atoms H	1 mol O $\Leftrightarrow$ 2 mol H

Recall that the symbol $\Leftrightarrow$ means "is chemically equivalent to" and that it is treated mathematically as an equal sign (see page 49 in Chapter 2).

TOOLS

Mole ratios

Within chemical compounds, moles of atoms always combine in the same ratio as the individual atoms themselves.

This tool allows us to use the atom-to-atom ratios in a chemical formula to easily prepare mole-to-mole conversion factors for calculations on the laboratory scale. For example, in the formula P_4O_{10}, the subscripts mean that there are 4 atoms of P for every 10 atoms of O in the molecule. On the laboratory scale, this also means that there are 4 moles of P for every 10 moles of O in 1 mole of this compound. We can relate P and O within the compound using the following conversion factors.

$$4 \text{ mol P} \Leftrightarrow 10 \text{ mol O} \qquad \text{from which we write} \qquad \frac{4 \text{ mol P}}{10 \text{ mol O}} \quad \text{or} \quad \frac{10 \text{ mol O}}{4 \text{ mol P}}$$

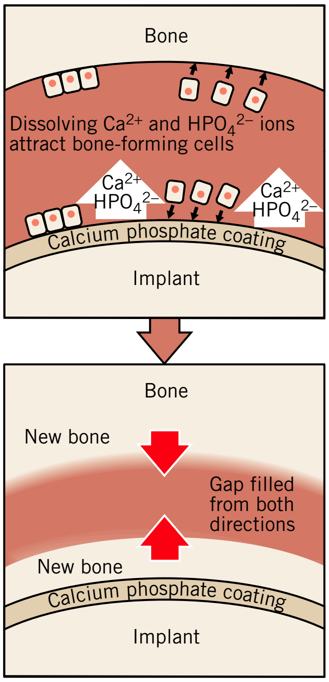
The formula P_4O_{10} also implies other equivalencies, each with its two associated conversion factors.

$$1 \text{ mol } \mathrm{P_4O_{10}} \Leftrightarrow 4 \text{ mol P} \quad \text{or} \quad \frac{1 \text{ mol } \mathrm{P_4O_{10}}}{4 \text{ mol P}} \quad \text{and} \quad \frac{4 \text{ mol P}}{1 \text{ mol } \mathrm{P_4O_{10}}}$$

$$1 \text{ mol } \mathrm{P_4O_{10}} \Leftrightarrow 10 \text{ mol O} \quad \text{or} \quad \frac{1 \text{ mol } \mathrm{P_4O_{10}}}{10 \text{ mol O}} \quad \text{and} \quad \frac{10 \text{ mol O}}{1 \text{ mol } \mathrm{P_4O_{10}}}$$

The following example illustrates how we use chemical formulas to develop mole ratios for calculations.

Example 4.5
Calculating the Amount of a Compound by Analyzing One Element


Bone
Dissolving Ca^{2+} and HPO_4^{2-} ions attract bone-forming cells
Ca^{2+} HPO_4^{2-}
Ca^{2+} HPO_4^{2-}
Calcium phosphate coating
Implant
Bone
New bone
Gap filled from both directions
New bone
Calcium phosphate coating
Implant

Some surfaces on bone implants are coated with calcium phosphate to permit the bone to actually bond to the surface.

Calcium phosphate is widely found in nature in the form of natural minerals. It is also found in bones and some kidney stones. In one case a sample is found to contain 0.864 moles of phosphorus. How many moles of $Ca_3(PO_4)_2$ are in that sample?

Analysis: Let's state the question in equation form first:

$$0.864 \text{ mol P} = ? \text{ mol } Ca_3(PO_4)_2$$

Since we start with moles of one substance and end with moles of a second, this is the appropriate place to use the mole ratio conversion factor.

Assembling the Tools: All we need is the mole ratio tool that relates P to the chemical formula $Ca_3(PO_4)_2$. We write it as

$$2 \text{ mol P} \Leftrightarrow 1 \text{ mol } Ca_3(PO_4)_2$$

Solution: Starting with the equation we expressed above, our tool is rearranged into a conversion factor so that the mol P cancels and we are left with the mol $Ca_3(PO_4)_2$. Applying that ratio we get

$$0.864 \ \cancel{\text{mol P}} \times \left(\frac{1 \text{ mol } Ca_3(PO_4)_2}{2 \ \cancel{\text{mol P}}}\right) = 0.432 \text{ mol } Ca_3(PO_4)_2$$

Is the Answer Reasonable? For a quick check, you can round 0.864 to 1 and divide by 2 to get 0.5. There is little difference between our estimate 0.5 and the calculated answer 0.432, and we conclude our answer is reasonable.

Practice Exercises

4.5 | Aluminum sulfate is analyzed, and the sample contains 0.0774 moles of sulfate ions. How many moles of aluminum are in the sample? (*Hint:* Recall the tool for writing the correct formula for aluminum sulfate.)

4.6 | How many moles of nitrogen atoms are combined with 8.60 mol of oxygen atoms in dinitrogen pentoxide?

Mass-to-Mass Calculations

TOOLS

Mass-to-mass conversions using formulas

One common use of stoichiometry in the lab occurs when we need to determine the mass of one reactant, B, needed to combine with a given mass of second reactant, A, to make a compound. These calculations are summarized by the following sequence of steps to convert the given mass of compound A to the mass of compound B.

$$\text{mass of A} \longrightarrow \text{moles of A} \longrightarrow \text{moles of B} \longrightarrow \text{mass of B}$$

In the following example we see how this is applied.

Example 4.6

Calculating the Amount of One Element from the Amount of Another in a Compound

Chlorophyll, the green pigment in leaves, has the formula $C_{55}H_{72}MgN_4O_5$. If 0.0011 g of Mg is available to a plant for chlorophyll synthesis, how many grams of carbon will be required to completely use up the magnesium?

Analysis: Let's begin, as usual, by restating the problem as follows.

$$0.0011 \text{ g Mg} \Leftrightarrow ?\text{ g C}$$

The tool on the preceding page shows the sequence of steps we use to relate the mass of one substance to the mass of another. Our first step is to convert the mass of Mg to moles of Mg. Once we know the moles of Mg, we can convert that to the moles of C using the formula of the compound. Finally, we can calculate the mass of the second substance, C, from the moles using the molar mass again. The sequence of calculations can be summarized as

$$0.0011 \text{ g Mg} \longrightarrow \text{mol Mg} \longrightarrow \text{mol C} \longrightarrow \text{g C}$$

Assembling the Tools: From the sequence of steps above we see that we will need the mass-to-moles tool to convert the mass of Mg to moles of Mg. The tool states that

$$24.3050 \text{ g Mg} = 1 \text{ mol Mg}$$

Next we need a mole ratio to convert moles of Mg to moles of C. This is

$$1 \text{ mol Mg} \Leftrightarrow 55 \text{ mol C} \quad \text{(these are exact numbers)}$$

In a problem that asks to convert the amount (grams, moles, or atomic scale units) of one substance into the amount of a different substance, the most important conversion factor is the mole-to-mole relationship between the two substances.

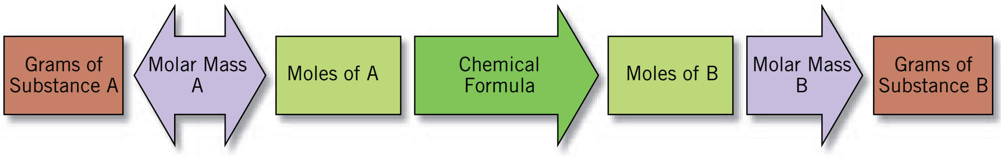
Finally, the mass-to-moles tool for carbon is

$$1 \text{ mol C} = 12.011 \text{ g C}$$

Our complete sequence for the problem, with numbers rounded to three significant figures, is

$$0.0011 \text{ g Mg} \xrightarrow{1 \text{ mol Mg} \Leftrightarrow 24.3 \text{ g Mg}} \text{mol Mg} \xrightarrow{1 \text{ mol Mg} \Leftrightarrow 55 \text{ mol C}} \text{mol C} \xrightarrow{1 \text{ mol C} \Leftrightarrow 12.0 \text{ g C}} \text{g C}$$

The general sequence for dealing with problems like the one we're solving here is illustrated below. The arrows indicate which tools are used for each conversion.



Solution: We now set up the solution by forming conversion factors so the units cancel.

$$0.0011\ \cancel{\text{g Mg}} \times \left(\frac{1\ \cancel{\text{mol Mg}}}{24.3\ \cancel{\text{g Mg}}}\right) \times \left(\frac{55\ \cancel{\text{mol C}}}{1\ \cancel{\text{mol Mg}}}\right) \times \left(\frac{12.0\ \text{g C}}{1\ \cancel{\text{mol C}}}\right) = 0.030\ \text{g C}$$

A plant cell must supply 0.030 g C for every 0.0011 g Mg to completely use up the magnesium in the synthesis of chlorophyll.

Is the Answer Reasonable? After checking that our units cancel properly, a quick estimate can be made by rounding all numbers to one significant figure. One way to do this results in the following expression (without units):

$$\frac{0.001 \times 1 \times 50 \times 10}{20 \times 1 \times 1} = \frac{0.5}{20} = \frac{0.05}{2} = 0.025$$

This value is close to the answer we got and gives us confidence that it is reasonable. (Note that if we rounded the 55 up to 60 our estimate would have been 0.030, which would still confirm our conclusion.)

Practice Exercises

4.7 | How many grams of iron are needed to combine with 25.6 g of O to make Fe_2O_3? (*Hint:* Recall the mole ratios that the formula represents.)

4.8 | An important iron ore called hematite contains iron(III) oxide. How many grams of iron are in a 15.0 g sample of hematite?

4.9 | Titanium(IV) oxide is the main pigment in white and other light-colored paints. How many grams of titanium will combine with 12.0 g of oxygen to form titanium(IV) oxide?

Percentage Composition

The usual form for describing the relative masses of the elements in a compound is a list of *percentages by mass* called the compound's **percentage composition.** The **percentage by mass** of an element is the number of grams of the element present in 100 g of the compound. In general, a percentage by mass is found by using the following equation.

TOOLS

Percentage composition

$$\text{Percentage by mass of element} = \frac{\text{mass of element}}{\text{mass of whole sample}} \times 100\% \qquad \textbf{(4.1)}$$

We can determine the percentage composition based on chemical analysis of a substance as shown in the next Example.

Example 4.7
Calculating a Percentage Composition from Chemical Analysis

A sample of a liquid with a mass of 8.657 g was decomposed into its elements and gave 5.217 g of carbon, 0.9620 g of hydrogen, and 2.478 g of oxygen. What is the percentage composition of this compound?

Analysis: Solving problems often requires that we know the meaning of key terms, in this case *percentage composition*. We have just discussed this term and now we can apply it in answering the question.

Assembling the Tools: The tool we need is expressed by Equation 4.1. We are given the mass of each element in the sample, and the sum of those masses gives us the mass of the whole sample. The total mass is 8.657 g and the individual masses are given.

Solution: Using Equation 4.1 for each of the elements in sequence gives three equations that we use to compute the needed percentages:

$$\text{For C:} \qquad \frac{5.217 \text{ g}}{8.657 \text{ g}} \times 100\% = 60.26\% \text{ C}$$

$$\text{For H:} \qquad \frac{0.9620 \text{ g}}{8.657 \text{ g}} \times 100\% = 11.11\% \text{ H}$$

$$\text{For O:} \qquad \frac{2.478 \text{ g}}{8.657 \text{ g}} \times 100\% = 28.62\% \text{ O}$$

Sum of percentages: 99.99%

One of the useful things about a percentage composition is that it tells us the mass of each of the elements in 100 g of the substance. For example, the results in this problem tell us that in 100.00 g of the liquid there are 60.26 g of carbon, 11.11 g of hydrogen, and 28.62 g of oxygen.

Is the Answer Reasonable? The "check" is that the percentages must add up to 100%, allowing for small differences caused by rounding. We can also check the individual results by rounding all the numbers to one significant figure to estimate the results. For example, the percentage C would be estimated as 5/9 × 100, which is a little over 50% and agrees with our answer.

Practice Exercises

4.10 | An organic compound weighing 0.6672 g is decomposed, giving 0.3481 g carbon and 0.0870 g hydrogen. What are the percentages of hydrogen and carbon in this compound? Is it likely that this compound contains another element? (*Hint:* Recall the tool concerning the conservation of mass.)

4.11 | When 0.5462 g of a compound was decomposed, 0.2012 g of nitrogen and 0.3450 g of oxygen were isolated. What is the percentage composition of this compound? Explain how you can determine if there are any other elements present in this compound.

We can also determine the percentage composition of a compound from its chemical formula. If we consider one mole of a substance, its molar mass will be the mass of the whole sample in Equation 4.1. The numerator in Equation 4.1 will be the mass associated with one of the elements in the formula. In the next section we see how this calculated percentage can be used as a physical property that is useful for identifying a substance.

Percentage Composition and Chemical Identity

We can use Equation 4.1 to determine the percentage composition of any chemical compound when we know its formula. Nitrogen and oxygen, for example, form all of the following compounds: N_2O, NO, NO_2, N_2O_3, N_2O_4, and N_2O_5. To identify an unknown sample of a compound of nitrogen and oxygen, one might compare the percentage composition found by experiment with the calculated, or theoretical, percentages for each possible formula. Which formula, for example, fits the percentage composition calculated in Practice Exercise 4.11? A strategy for matching formulas with mass percentages is outlined in the following example.

Example 4.8
Identifying a Compound Based on Percentage Composition

Do the mass percentages of 25.94% N and 74.06% O match the formula N_2O_5?

Analysis: To calculate the mass percentages we need to use Equation 4.1. Looking at the equation, we will need the masses of N, O, and N_2O_5 in a sample of the compound. *If we choose 1 mol of the given compound to be this sample, it will be easy to determine the mass of the oxygen, nitrogen, and dinitrogen pentoxide that make up one mole of* N_2O_5.

Assembling the Tools: We need Equation 4.1 to calculate the percent composition. We will need the tool for calculating the molar mass of N_2O_5 and the mole ratios we can obtain from that formula. We need to perform a mass-to-moles conversion for nitrogen and oxygen atoms.

The required relationships are:

$$\begin{aligned} 2 \text{ mol N} &\Leftrightarrow 1 \text{ mol } N_2O_5 \\ 5 \text{ mol O} &\Leftrightarrow 1 \text{ mol } N_2O_5 \\ 1 \text{ mol N} &= 14.01 \text{ g N} \\ 1 \text{ mol O} &= 16.00 \text{ g O} \end{aligned}$$

Solution: We know that 1 mol of N_2O_5 must contain 2 mol N and 5 mol O from the mol ratio tool. The corresponding number of grams of N and O are found as follows.

$$1 \ \cancel{\text{mol } N_2O_5} \times \frac{2 \ \cancel{\text{mol N}}}{1 \ \cancel{\text{mol } N_2O_5}} \times \frac{14.01 \text{ g N}}{1 \ \cancel{\text{mol N}}} = 28.02 \text{ g N}$$

$$1 \ \cancel{\text{mol } N_2O_5} \times \frac{5 \ \cancel{\text{mol O}}}{1 \ \cancel{\text{mol } N_2O_5}} \times \frac{16.00 \text{ g O}}{1 \ \cancel{\text{mol O}}} = 80.00 \text{ g O}$$

$$1 \text{ mol } N_2O_5 = 108.02 \text{ g } N_2O_5$$

Now we can calculate the percentages.

$$\text{For \% N:} \qquad \frac{28.02 \text{ g}}{108.02 \text{ g}} \times 100\% = 25.94\% \text{ N in } N_2O_5$$

$$\text{For \% O:} \qquad \frac{80.00 \text{ g}}{108.02 \text{ g}} \times 100\% = 74.06\% \text{ O in } N_2O_5$$

Thus the experimental values do match the theoretical percentages for the formula N_2O_5.

Is the Answer Reasonable? The easiest check for this problem is to be sure that all percentages add up to 100%. They do add to 100% and so the calculated result is reasonable.

Practice Exercises

4.12 | Calculate the theoretical percentage composition of N_2O_4. (*Hint:* Recall the definition of percentage composition.)

4.13 | Calculate the theoretical percentage compositions for N_2O, NO, NO_2, N_2O_3, N_2O_4, and N_2O_5. Which of these compounds produced the data in Practice Exercise 4.11?

In working Practice Exercise 4.13, you may have noticed that the percentage composition of NO_2 was the same as that of N_2O_4. This is because both compounds have the same mole ratio. All compounds with the same mole ratios will have the same percentage compositions.

4.3 | Determining Empirical and Molecular Formulas

One of the major activities of chemists is to synthesize compounds that have never existed before. In pharmaceutical research, chemists often synthesize entirely new compounds, or isolate new compounds from plant and animal tissues. They must then determine the formula and structure of the new compound. Modern chemists use mass spectroscopy and other moderrn instruments for structure analysis. However, they still rely upon elemental analysis, where the compound is decomposed chemically to find the masses of elements within a given amount of compound to determine *empirical formulas*. Let's see how such experimental mass measurements, expressed in a variety of ways, can be used to determine these formulas.

A form of the element phosphorus known as "white phosphorus" is *pyrophoric*—that is, it spontaneously burns when exposed to air. The compound that forms when phosphorus burns in oxygen consists of molecules with the formula P_4O_{10}. When a formula gives the composition of one *molecule*, it is called a **molecular formula**. Notice, however, that both the subscripts 4 and 10 are divisible by 2, so the *smallest* numbers that tell us the *ratio* of P to O are 2 and 5. We can write a simpler (but less informative) formula that expresses this ratio, P_2O_5. This is called the **empirical formula** because it can also be obtained from an experimental analysis of the compound.

> The empirical formula expresses the simplest ratio of the atoms of each element in a compound.

TOOLS

Empirical formulas

We already know that the ratio of atoms in a compound is the same as a ratio of the moles of those atoms in the compound. We will determine the simplest ratio of moles from experimental data. The experimental data we need is any information that allows us to determine the moles of each element in a sample of the compound. We will investigate three types of data that can be used to determine empirical formulas. They are (a) masses of the elements, (b) percentage composition, and (c) combustion data. In all three, the goal is to obtain the simplest ratio of moles of each element in the formula.

Empirical Formulas from Mass Data

If we determine the mass of each element in a pure sample of a compound we can calculate the moles of each element. From that we can find the simplest ratio of moles, which by definition is the empirical formula. In many instances, we can analyze a sample for all but one element and then use the law of conservation of mass to calculate the missing mass, as shown in the next example.

Example 4.9

Calculating an Empirical Formula from Mass Data

A 2.57 g sample of a compound composed of only tin and chlorine was found to contain 1.17 g of tin. What is the compound's empirical formula?

■ **Analysis:** The subscripts in an empirical formula can be interpreted as the relative number of moles of the elements in a compound. If we can find the *mole* ratio of Sn to Cl, we will have the empirical formula. The first step, therefore, is to convert the numbers of grams of Sn and Cl to the numbers of moles of Sn and Cl. Then we convert these numbers into their simplest positive *whole-number,* or *integer,* ratio.

■ The word integer is synonymous with whole number. Integers are never fractions or decimal numbers. Exact numbers are often integers.

The problem did not give the mass of chlorine in the 2.57 g sample. However, we can calculate it using the tool that expresses the law of conservation of mass.

■ **Assembling the Tools:** The law of conservation of mass, one of our tools from Chapter 1, requires that the mass of compound equal the sum of the mass of Cl and the mass of Sn.

$$2.57 \text{ g compound} = \text{mass of Cl} + 1.17 \text{ g Sn}$$

The molar mass is the tool that allows us to calculate the moles of each element.

$$118.7 \text{ g Sn} = 1 \text{ mol Sn}$$
$$35.45 \text{ g Cl} = 1 \text{ mol Cl}$$

■ **Solution:** First, we find the mass of Cl in 2.57 g of compound:

$$\text{Mass of Cl} = 2.57 \text{ g compound} - 1.17 \text{ g Sn} = 1.40 \text{ g Cl}$$

Now we use the molar mass equalities to create ratios to convert the mass data for tin and chlorine into moles.

$$1.17 \cancel{\text{g Sn}} \times \frac{1 \text{ mol Sn}}{118.7 \cancel{\text{g Sn}}} = 0.00986 \text{ mol Sn}$$

$$1.40 \cancel{\text{g Cl}} \times \frac{1 \text{ mol Cl}}{35.45 \cancel{\text{g Cl}}} = 0.0395 \text{ mol Cl}$$

We could now write a formula: $Sn_{0.00986}Cl_{0.0395}$, which does express the mole ratio, but subscripts also represent atom ratios and need to be integers. To convert the decimal subscripts to integers, we begin by dividing each by the smallest number in the set. *This is always the way to begin the search for whole-number subscripts; pick the smallest number of the set as the divisor.* It's guaranteed to make at least one subscript a whole number—namely, 1. Here, we divide both numbers by 0.00986.

$$Sn_{\frac{0.00986}{0.00986}}Cl_{\frac{0.0395}{0.00986}} = Sn_{1.00}Cl_{4.01}$$

In most cases if, after this step, a calculated subscript differs from a whole number by less than 0.1, we can safely round to the nearest whole number. We may round 4.01 to 4, so the empirical formula is $SnCl_4$.

■ **Is the Answer Reasonable?** In addition to the fact that whole-number subscripts were easily found, you should also recall from Chapter 3 that tin forms either the Sn^{2+} or the Sn^{4+} ion and that chlorine forms only the Cl^- ion. Therefore either $SnCl_2$ or $SnCl_4$ is a reasonable compound, and one of them was our answer.

Practice Exercises

4.14 | A 1.525 g sample of a compound between nitrogen and oxygen contains 0.712 g of nitrogen. Calculate its empirical formula. (*Hint:* How many grams of oxygen are there?)

4.15 | A 1.525 g sample of a compound between sulfur and oxygen was prepared by burning 0.7625 g of sulfur in air and collecting the product. What is the empirical formula for the compound formed?

Sometimes our strategy of using the lowest common divisor does not give whole numbers. If a decimal value corresponding to a rational fraction results, we can obtain integers by multiplying by the denominator of the rational fraction. Let's see how to handle such a situation.

Example 4.10
Calculating an Empirical Formula from Mass Composition

One of the compounds of iron and oxygen, "black iron oxide," occurs naturally in the mineral magnetite. When a 2.448 g sample was analyzed it was found to have 1.771 g of Fe and 0.677 g of O. Calculate the empirical formula of this compound.

The mineral magnitite like any magnet, is able to affect the orientation of a compass needle. *(Visuals Unlimited)*

Analysis: We are given the masses of both iron and oxygen and we need to convert these masses into moles using their atomic masses. Finally, we need to obtain the simplest whole-number ratio of the moles of the elements to use as subscripts in the empirical formula.

Assembling the Tools: The moles of each element are obtained from a mass-to-moles conversion using the equalities:

$$1 \text{ mol Fe} = 55.845 \text{ g Fe} \quad \text{and} \quad 1 \text{ mol O} = 16.00 \text{ g O}$$

We then follow the procedure above for obtaining integer subscripts. If we do not get integers (within ± 0.1) we will need to find the rational fraction that corresponds to the decimal portion of the number and multiply by its denominator.

Solution: The moles of Fe and O in the sample are calculated.

$$1.771\ \cancel{\text{g Fe}} \times \frac{1 \text{ mol Fe}}{55.845\ \cancel{\text{g Fe}}} = 0.03171 \text{ mol Fe}$$

$$0.677\ \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00\ \cancel{\text{g O}}} = 0.0423 \text{ mol O}$$

These results let us write the formula as $Fe_{0.03171}O_{0.0423}$.

Our first effort to change the ratio of 0.03171 to 0.0423 into whole numbers is to divide both by the smallest number, 0.03171.

$$Fe_{\frac{0.03171}{0.03171}}O_{\frac{0.0423}{0.03171}} = Fe_{1.000}O_{1.33}$$

Table 4.1 Decimal and Rational Fractions	
Decimal	**Fraction**[a]
0.20	1/5
0.25	1/4
0.33	1/3
0.40	2/5
0.50	1/2
0.60	3/5
0.66	2/3
0.75	3/4
0.80	4/5

[a] Use the denominator of the fraction as a multiplier to create whole-number subscripts in empirical formulas.

This time we cannot round 1.33 to 1.0 because the decimal we want to round, 0.33, is larger than the 0.1 criterion established previously. The subscript for O, 1.33, is much too far from a whole number to round off. In a *mole* sense, the ratio of 1 to 1.33 is correct; we just need a way to re-state this ratio in whole numbers. To do this, we need to recognize that the decimal 0.33 represents 1/3 (one-third). The denominator is 3, and if we multiply both subscripts by 3 we will get

$$Fe_{(1.000 \times 3)}O_{(1.33 \times 3)} = Fe_{3.000}O_{3.99}$$

or a formula of Fe_3O_4. Table 4.1 in the margin lists some common decimals and their related fractions.

TOOLS

Determination of integer subscripts

A less mathematical method that works is to use trial and error. First, multiply all subscripts by 2; if that does not give integer subscripts, go back and try 3, then 4, 5, and so on. In this example you would have found integer subscripts after multiplying by 3.

Is the Answer Reasonable? One way to check our answer is to estimate the percentage of iron from the given data and from our result. The given data for iron is 1.771 g Fe and the whole sample weighs 2.448 g. The percentage iron is estimated as:

$$\frac{1.771 \text{ g}}{2.448 \text{ g}} \times 100 \approx \frac{\mathbf{1.8\ g}}{\mathbf{2.4\ g}} \times \mathbf{100} = \frac{3}{4} \times 100 = \text{approximately } 75\%$$

In one mole of the compound Fe_3O_4, the mass of iron is $3 \times 55.8 = 167.4$ and the molar mass is 231.4. The percentage of iron is estimated as:

$$\frac{167.4\ \text{g}}{231.4\ \text{g}} \times 100 \approx \frac{170\ \text{g}}{230\ \text{g}} \times 100 = \frac{\mathbf{1.7\ g}}{\mathbf{2.3\ g}} \times \mathbf{100} = \text{approximately } 75\%$$

We don't have to do any calculations because we can see that mathematical expressions from both calculations are almost the same, and the answers will be very close to each other. Let's compare the bold term from each equation:

$$\frac{1.8\ \text{g}}{2.4\ \text{g}} \times 100 \approx \frac{1.7\ \text{g}}{2.3\ \text{g}} \times 100$$

We are able to conclude that our percentages of iron are the same and our empirical formula is reasonable.

Practice Exercises

4.16 | When aluminum is produced by electrolysis we get 5.68 tons of aluminum and 5.04 tons of oxygen. What is the empirical formula of the compound that is being electrolyzed? (*Hint:* 1 ton = 2000 lb and 1 lb = 454 g.)

4.17 | A 2.012 g sample of a compound of nitrogen and oxygen has 0.522 g of nitrogen. Calculate its empirical formula.

Empirical Formulas from Experimental Mass Percentages

TOOLS

Empirical formulas from percentage composition

Only rarely is it possible to obtain the masses of every element in a compound by the use of just one weighed sample. Two or more analyses carried out on different samples are often needed. For example, suppose an analyst is given a compound known to consist exclusively of calcium, chlorine, and oxygen. The mass of calcium in one weighed sample and the mass of chlorine in another sample would be determined in separate experiments. Then the mass data for calcium and chlorine would be converted to percentages by mass *so that the data from different samples relate to the same sample size, namely, 100 g of the compound.* The percentage of oxygen would be calculated by difference because % Ca + % Cl + % O = 100%. If we consider a 100 g sample of our compound, each mass percentage of an element would represent the number of grams of that element in the sample. From here, the masses are next converted into the corresponding number of moles of each element. Finally, mole proportions are converted to integers in the way we just studied, giving us the subscripts for the empirical formula. Let's see how this works.

Example 4.11
Calculating an Empirical Formula from Percentage Composition

A white powder used in paints, enamels, and ceramics has the following percentage composition: Ba, 69.6%; C, 6.09%; and O, 24.3%. What is its empirical formula? What is the name of this compound?

■ **Analysis:** Consider having 100 grams of this compound. The percentages of the elements given in the problem are numerically the same as the masses of these elements in a 100 g sample.

Now that we have the masses of the elements we can calculate the moles of each element and then the integer values for the subscripts as we did in the previous examples.

■ We see a general principle that by assuming a 100 g sample, all percent signs can be easily changed to gram units for our calculations.

Assembling the Tools: We will need the molar mass as our tool to determine the moles of each element. We will also need the procedures for finding integer subscripts.

Solution: Assuming a 100 g sample of the compound, we quickly convert 69.6% Ba to 69.6 g Ba, 6.09% C to 6.09 g C, and 24.3% O to 24.3 g O. Now these masses are converted to moles.

$$\text{Ba:} \quad 69.6\ \cancel{\text{g Ba}} \times \frac{1\ \text{mol Ba}}{137.3\ \cancel{\text{g Ba}}} = 0.507\ \text{mol Ba}$$

$$\text{C:} \quad 6.09\ \cancel{\text{g C}} \times \frac{1\ \text{mol C}}{12.01\ \cancel{\text{g C}}} = 0.507\ \text{mol C}$$

$$\text{O:} \quad 24.3\ \cancel{\text{g O}} \times \frac{1\ \text{mol O}}{16.00\ \cancel{\text{g O}}} = 1.52\ \text{mol O}$$

Our preliminary empirical formula is then

$$\text{Ba}_{0.507}\text{C}_{0.507}\text{O}_{1.52}$$

We next divide each subscript by the smallest value, 0.507.

$$\text{Ba}_{\frac{0.507}{0.507}}\text{C}_{\frac{0.507}{0.507}}\text{O}_{\frac{1.52}{0.507}} = \text{Ba}_{1.00}\text{C}_{1.00}\text{O}_{3.00}$$

The subscripts are whole numbers, so the empirical formula is $BaCO_3$, representing barium carbonate.

Is the Answer Reasonable? First of all, we found simple, whole-number, subscripts, which strongly suggest that the answer is right. In addition, our knowledge of ionic compounds and the polyatomic ions from Chapter 3 tells us that the combination of a barium ion, Ba^{2+}, and the carbonate ion, CO_3^{2-}, yields the same formula, $BaCO_3$. We can conclude that our answer is reasonable.

Practice Exercises

4.18 | A white solid used to whiten paper has the following percentage composition: Na, 32.4%; S, 22.6%. The unanalyzed element is oxygen. What is the compound's empirical formula? (*Hint:* What law allows you to calculate the % oxygen?)

4.19 | Cinnamon gets some of its flavor from cinnamaldehyde that is 81.79% C; 6.10% H and the rest is oxygen. Determine the empirical formula for this compound.

The law of conservation of mass and its use with percentage composition is important because it allowed us to determine the amount of three substances using only two experiments. This in itself is a considerable saving in time and effort. Additionally, it is often difficult to analyze a sample for certain elements, oxygen for example, and using percentage measurements helps avoid this problem.

Empirical Formulas from Indirect Analysis

In practice, a compound is seldom broken down completely to its *elements* in a quantitative analysis. Instead, the compound is changed into other *compounds*. The reactions separate the elements by capturing each one entirely (quantitatively) in a *separate* compound *whose formula is known*.

In Example 4.12, we illustrate the indirect analysis of a compound made entirely of carbon, hydrogen, and oxygen. Such compounds burn completely in pure oxygen—it is called a *combustion reaction*—and the sole products are carbon dioxide and water. (This particular kind of indirect analysis is sometimes called a **combustion analysis.**) The complete

ON THE CUTTING EDGE 4.1

Combustion Analysis

Determining the mass of carbon and hydrogen in a compound can be done by burning the compound in pure oxygen in the presence of substances called catalysts that ensure complete conversion of carbon to CO_2 and hydrogen to H_2O. The stream of gases passes through a pre-weighed tube containing anhydrous calcium sulfate and then through a second pre-weighed tube containing sodium hydroxide. The first tube absorbs the water and the second absorbs the carbon dioxide, as seen in Figure 1.

The increase in masses of these tubes represents the masses of CO_2 and H_2O from which the masses of carbon and hydrogen can be calculated. If a compound contains oxygen, it would be determined by subtracting the mass of hydrogen and carbon from the total mass burned. Compounds containing nitrogen, sulfur, or a halogen are more difficult to analyze and often require additional time-consuming experiments.

Modern instruments automate the process of analyzing the combustion products using a technique called gas chromatography. After burning a weighed sample, advanced catalysts make sure that all the carbon, nitrogen, and sulfur atoms are converted to CO_2, N_2, and SO_2. One instrument automatically takes a small sample of the gases and injects it into a gas chromatograph. Within the instrument the gases travel through a tubular column packed with absorbents that cause each gas to travel at a different rate. At the end of the column a thermal conductivity detector, which measures the ability of a gas to dissipate heat, senses each component of the mixture. The result is a chromatogram with a peak for each separate substance, as shown in Figure 2.

The area of each peak is proportional to the amount of each gas, and the internal computer computes the percentage composition. Very pure compounds, called standards, with known percentages of each element are burned to calibrate the instrument.

All instruments require standard samples of high purity and known composition to calibrate the readout. Typically, the classical method takes about 30 minutes per sample, and the instruments, once calibrated, take between 2 and 5 minutes per sample.

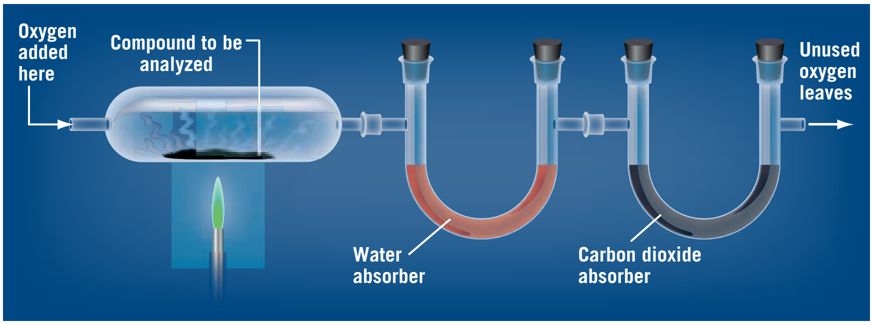


Figure 1 Classic CH analysis. This experimental setup shows pure oxygen added to the compound. Combustion products are absorbed by reaction with chemicals in the U-tubes. Calcium sulfate absorbs water and sodium hydroxide absorbs carbon dioxide.

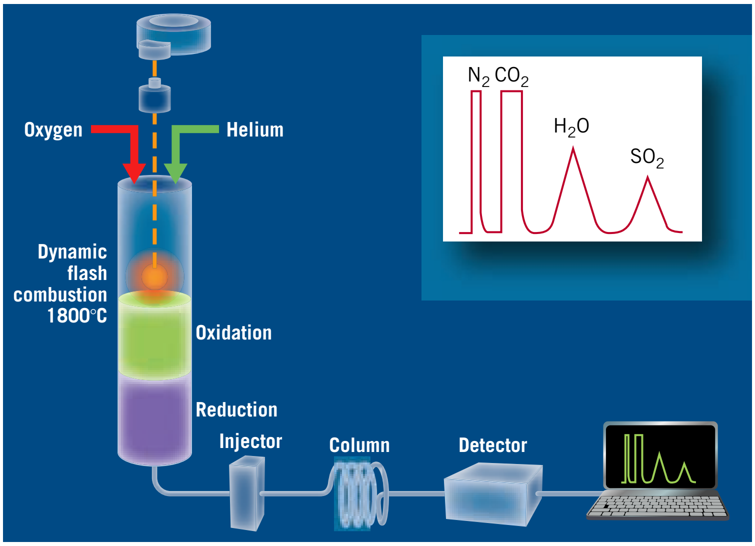


Figure 2 Diagram of an automated CHNS elemental analysis system. The diagram illustrates the combustion chamber, the chromatography column, a thermal conductivity detector, and a sample of a chromatogram with peaks for N_2, CO_2, H_2O, and SO_2.

Figure 3 Elemental analysis using gas chromatography. Modern CHN analyzer. *(© 2010 PerkinElmer, Inc. All rights reserved.)*

combustion of methyl alcohol (CH_3OH), for example, occurs according to the following equation.

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

The carbon dioxide and water can be separated and are individually weighed. Notice that all of the carbon atoms in the original compound end up among the CO_2 molecules, and all of the hydrogen atoms are in H_2O molecules. In this way at least two of the original elements, C and H, are quantitatively measured.

We will calculate the mass of carbon in the CO_2 collected, which equals the mass of carbon in the original sample. Similarly, we will calculate the mass of hydrogen in the H_2O collected, which equals the mass of hydrogen in the original sample. When added together, the mass of C and mass of H are less than the total mass of the sample because part of the sample is composed of oxygen. The law of conservation of mass allows us to subtract the sum of the C and H masses from the original sample mass to obtain the mass of oxygen in the sample of the compound.

Example 4.12
Empirical Formula from Indirect Analysis

A 0.5438 g sample of a pure liquid consisting of only C, H, and O was burned in 100% oxygen, and 1.039 g of CO_2 and 0.6369 g of H_2O were obtained. What is the empirical formula of the compound?

■ **Analysis:** There are several parts to this problem; let's look at a logical sequence of what we have to do. First, we need to calculate the mass of the elements, C and H, by determining the number of grams of C in the CO_2 and the number of grams of H in the H_2O. Then the mass of oxygen is determined by difference. Next, we use the masses of C, H, and O to calculate the moles of each. Finally, we use our procedures to convert the moles of each element into integer subscripts in the empirical formula.

■ **Assembling the Tools:** To convert the masses of CO_2 and H_2O to grams of C and H we will need our tools for converting between mass and moles. In this problem we start with the equalities:

$$1 \text{ mol C} = 12.011 \text{ g C}$$
$$1 \text{ mol CO}_2 = 44.010 \text{ g CO}_2$$
$$1 \text{ mol O} = 15.999 \text{ g O}$$
$$1 \text{ mol H}_2\text{O} = 18.015 \text{ g H}_2\text{O}$$

Next we need the mole ratio equivalencies that we derive from the formulas.

$$1\ \text{mol C} \Leftrightarrow 1\ \text{mol CO}_2$$
$$2\ \text{mol H} \Leftrightarrow 1\ \text{mol H}_2\text{O}$$

This is similar to the calculations in Example 4.6, where we use the normal conversion sequence from grams of compound to grams of an element in the compound. We then need the law of conservation of mass,

$$\text{Mass of compound} = \text{mass of C} + \text{mass of H} + \text{mass of O}$$

to determine the oxygen content.

After we have the mass of each element, we will convert all the masses to moles. The final step is to convert the calculated moles of each element into an integer subscript for our formula.

Solution: First, we find the number of grams of C in the CO_2 as

$$1.039\ \cancel{\text{g CO}_2} \times \frac{1\ \cancel{\text{mol CO}_2}}{44.009\ \cancel{\text{g CO}_2}} \times \frac{1\ \cancel{\text{mol C}}}{1\ \cancel{\text{mol CO}_2}} \times \frac{12.011\ \text{g C}}{1\ \cancel{\text{mol C}}} = 0.2836\ \text{g C}$$

For the number of grams of H in 0.6369 g of H_2O we calculate

$$0.6369\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.015\ \cancel{\text{g H}_2\text{O}}} \times \frac{2\ \cancel{\text{mol H}}}{1\ \cancel{\text{mol H}_2\text{O}}} \times \frac{1.0079\ \text{g}}{1\ \cancel{\text{mol H}}} = 0.07127\ \text{g H}$$

The total mass of C and H is therefore the sum of these two quantities.

$$\text{Total mass of C and H} = 0.2836\ \text{g C} + 0.07127\ \text{g H} = 0.3549\ \text{g}$$

The difference between this total and the 0.5438 g mass of the original sample is the mass of oxygen (the only other element present).

$$\text{Mass of O} = 0.5438\ \text{g} - 0.3549\ \text{g} = 0.1889\ \text{g O}$$

Now we can convert the masses of the elements to an empirical formula.

$$\text{For C:}\quad 0.2836\ \cancel{\text{g C}} \times \frac{1\ \cancel{\text{mol C}}}{12.011\ \text{g C}} = 0.02361\ \text{mol C}$$

$$\text{For H:}\quad 0.07127\ \cancel{\text{g H}} \times \frac{1\ \text{mol H}}{1.0079\ \cancel{\text{g H}}} = 0.07071\ \text{mol H}$$

$$\text{For O:}\quad 0.1889\ \cancel{\text{g O}} \times \frac{1\ \text{mol O}}{15.999\ \cancel{\text{g O}}} = 0.01181\ \text{mol O}$$

Our preliminary empirical formula is thus $C_{0.02361}H_{0.070701}O_{0.01181}$. We divide all of these subscripts by the smallest number, 0.01181.

$$C_{\frac{0.02361}{0.01181}}H_{\frac{0.070701}{0.01181}}O_{\frac{0.01181}{0.01181}} = C_{1.999}H_{5.987}O_1$$

The results are acceptably close to integers, to conclude that the empirical formula is C_2H_6O.

Is the Answer Reasonable? Our checks on problems need to be quick and efficient. The fact that the integer subscripts were found easily suggests that the answer is correct and we can usually stop here. If more confirmation is needed, we can estimate the answers to the individual steps.

Practice Exercises

4.20 | A sample containing only sulfur and carbon is completely burned in air. The analysis produced 0.640 g of SO_2 and 0.220 g of CO_2. What is the empirical formula? (*Hint:* Use the tools for relating grams of a compound to grams of an element.)

4.21 | The combustion of a 5.048 g sample of a compound of C, H, and O gave 7.406 g of CO_2 and 3.027 g of H_2O. Calculate the empirical formula of the compound.

Molecular Formulas from Empirical Formulas and Molecular Masses

The empirical formula is the accepted formula unit for ionic compounds. For molecular compounds, however, chemists prefer *molecular* formulas because they give the number of atoms of each type in a molecule, rather than just the simplest ratio of moles of elements in a compound as the empirical formula does.

Sometimes an empirical and molecular formula are the same. Two examples are H_2O and NH_3. When they are different, the subscripts of the molecular formula are integer multiples of those in the empirical formula. The subscripts of the molecular formula P_4O_{10}, for example, are each two times those in the empirical formula, P_2O_5, as you saw earlier. The molecular mass of P_4O_{10} is likewise two times the empirical formula mass of P_2O_5. This observation provides us with a way to find out the molecular formula for a compound provided we have a way of determining experimentally the molecular mass of the compound. If the experimental molecular mass *equals* the calculated empirical formula mass, the empirical formula is the same as the molecular formula. Otherwise, the molecular mass will be a whole-number multiple of the empirical formula mass. Whatever the integer is, it's a common multiplier for the subscripts of the empirical formula.

■ There are many simple methods for determining molecular masses. They are discussed in Chapters 11 and 13. Instruments such as the mass spectrometers discussed in Chapter 3 can also be used.

Example 4.13

Determining a Molecular Formula from an Empirical Formula and a Molecular Mass

Styrene, the raw material for polystyrene foam plastics, has an empirical formula of CH. Its molecular mass is 104. What is its molecular formula?

■ **Analysis:** Since we know the empirical formula and the molar mass of the compound, styrene, we need to find out how many empirical formula units make up one molecule. Then the molecular formula will have subscripts that are an integer multiple of the empirical formula subscripts.

■ **Assembling the Tools:** The relationship between empirical and molecular formulas tells us that the molecular mass of styrene, 104, divided by the formula mass of the empirical formula, CH, will result in an integer that represents the number of empirical formula units in the molecule itself.

$$\frac{\text{Molecular mass of styrene}}{\text{Empirical formula mass of CH}} = \text{integer}$$

To obtain the molecular formula, all subscripts of the empirical formula are multiplied by that integer.

■ **Solution:** For the empirical formula, CH, the formula mass is

$$12.01 + 1.008 = 13.02$$

To find how many CH units weighing 13.02 are in a mass of 104, we divide.

$$\frac{104}{13.02} = 7.99$$

Rounding this to 8, we find that eight CH units make up the molecular formula of styrene, and styrene must have subscripts 8 times those in CH. Styrene, therefore, is C_8H_8.

■ **Is the Answer Reasonable?** The molecular mass of C_8H_8 is approximately $(8 \times 12) + (8 \times 1) = 104$, which is consistent with the molecular mass we started with.

Practice Exercises

4.22 | After determining that the empirical formulas of two different compounds were CH_2Cl and CHCl, a student mixed up the data for the molecular masses. However, the student knew that one compound had a molecular mass of 100 and the other had a molecular mass of 289. What are the likely molecular formulas of the two compounds? (*Hint:* Recall the relationship between the molecular and empirical formula.)

4.23 | The empirical formula of hydrazine is NH_2 and its molecular mass is 32.0. What is its molecular formula?

4.4 | The Mole and Chemical Reactions

Writing and Balancing Chemical Equations

Here we will see that a *balanced* chemical equation is a very useful tool for problem solving. We learned in Chapters 1 and 3 that a *chemical equation* is a shorthand, quantitative description of a chemical reaction. An equation is balanced when all atoms present among the reactants (written to the left of the arrow) are also somewhere among the products (written to the right of the arrow). Coefficients, numbers placed in front of formulas, are multiplier numbers for their respective formulas that are used to balance an equation.

Always approach the balancing of an equation as a two-step process.

Step 1. *Write the unbalanced "equation."* Organize the formulas in the pattern of an equation with plus signs and an arrow (think of the arrow as an equal sign because we need to end up with the same number of each atom on both sides). Use *correct* formulas. (You learned to write many of them in Chapter 3, but until we have studied more chemistry, you will usually be given formulas.)

Step 2. *Adjust the coefficients to get equal numbers of each kind of atom on both sides of the arrow.* When doing Step 2, make no changes in the formulas, either in the atomic symbols or their subscripts. If you do, the equation will involve different substances from those intended. It often helps to start the process with the most complex formula, leaving elements and simple compounds to the end.

Zinc metal reacts with hydrochloric acid. *(Richard Megna/Fundamental Photographs)*

We'll begin with simple equations that can be balanced easily by inspection. An example is the reaction of zinc metal with hydrochloric acid (see the margin photo). First, we need the correct formulas, and this time we'll include the physical states because they may not be obvious. The reactants are zinc, Zn(*s*), and hydrochloric acid, an aqueous solution of the gas hydrogen chloride, HCl, symbolized as HCl(*aq*). We also need formulas for the products. Zn changes to a water-soluble compound, zinc chloride, $ZnCl_2(aq)$, and hydrogen gas, $H_2(g)$, bubbles out as the other product. (Recall that hydrogen is one of the elements that occurs naturally as a *diatomic molecule*, not as an atom.)

Step 1. Write an unbalanced equation.

$$Zn(s) + HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g) \qquad \text{(unbalanced)}$$

Step 2. Adjust the coefficients to get equal numbers of each kind of atom on both sides of the arrow.

There is no simple set of rules for adjusting coefficients—as you may have discovered, experience is the greatest help. Experience has taught chemists that the following guidelines often get to the solution most directly when they are applied in the order given.

Some Guidelines for Balancing Equations

1. Start balancing with the most complicated formula first. Elements, particularly H_2 and O_2, should be left until the end.
2. Balance atoms that appear in only two formulas: one as a reactant and the other as a product. (Leave elements that appear in three or more formulas until later.)
3. Balance as a group those polyatomic ions that appear unchanged on both sides of the arrow.

TOOLS

Balancing chemical equations

Using the guidelines given here, we'll leave the Zn(*s*) and $H_2(g)$ until later. The two remaining formulas have chlorine in common. Because there are two Cl to the right of the arrow but only one to the left, we put a 2 in front of the HCl on the left side. Remember that this also sets the coefficient of $ZnCl_2$ as 1, which by custom is not written. The result is

$$\mathrm{Zn}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

We then balance the hydrogen and zinc and find that no additional coefficient changes are needed. Everything is now balanced. On each side we find 1 Zn, 2 H, and 2 Cl. One complication is that an infinite number of *balanced* equations can be written for any given reaction! We might, for example, have adjusted the coefficients so that our equation came out as follows.

$$2\mathrm{Zn}(s) + 4\mathrm{HCl}(aq) \longrightarrow 2\mathrm{ZnCl_2}(aq) + 2\mathrm{H_2}(g)$$

This equation is also balanced. For simplicity, chemists prefer the *smallest* whole-number coefficients when writing balanced equations.

■ Although the smallest whole-number coefficients are preferred, stoichiometric calculations still work as long as the equation is balanced.

Example 4.14

Writing a Balanced Equation

Sodium hydroxide and phosphoric acid, H_3PO_4, react as aqueous solutions to give sodium phosphate and water. The sodium phosphate remains in solution. Write the balanced equation for this reaction.

■ **Analysis:** First, we need to write an unbalanced equation that includes the reactant formulas on the left-hand side and the product formulas on the right. Then we need to use the above procedures for balancing the equation.

■ **Assembling the Tools:** We are given the formula only for phosphoric acid. We need to use the nomenclature tools in Chapter 3 to determine that the formula of sodium hydroxide is NaOH; water is H_2O, and sodium phosphate has a formula of Na_3PO_4. Finally, we use our guidelines for balancing equations.

■ **Solution:** We write the unbalanced equation by placing all the reactants to the left of the arrow and all products to the right. The designation (*aq*) is added for all substances dissolved in water (except H_2O itself; we'll not give it any designation when it is in its liquid state).

$$\mathrm{NaOH}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{Na_3PO_4}(aq) + \mathrm{H_2O} \qquad \text{(unbalanced)}$$

■ When a reaction occurs in aqueous solution, water is not pure water and the (*l*) is inappropriate. Also, the term (*aq*) is meaningless since we would be saying "an aqueous solution of water." In solution chemistry, therefore the state of water is not specified.

We will focus on balancing the Na and P atoms first, since H and O atoms appear in more than two formulas. Focusing on the Na first, there are 3 Na on the right side, so we put a 3 in front of NaOH on the left, as a trial. Remember that this step also places an unwritten 1 in front of the Na_3PO_4 formula.

$$3\mathrm{NaOH}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{Na_3PO_4}(aq) + \mathrm{H_2O} \qquad \text{(unbalanced)}$$

Now that the Na are in balance we can focus on the P. Since all of the phosphorus is found in the PO_4 units, we will balance the phosphate units as a group of atoms rather than individually. We see that the PO_4 unit is already balanced and that means that the H_3PO_4 has a coefficient of 1. Only the coefficient for water has not been assigned. We can see that the reactant side has 6 H and 3 O atoms (notice that we don't count the oxygen atoms in the PO_4 units since they have already been balanced), which will produce 3 H_2O molecules. Thus the coefficient of water should be three.

$$3NaOH(aq) + H_3PO_4(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O \qquad \text{(balanced)}$$

We now have a balanced equation.

■ **Is the Answer Reasonable?** On each side we have 3 Na, 1 PO_4, 6 H, and 3 O besides those in PO_4, and since the coefficients for $H_3PO_4(aq)$ and $Na_3PO_4(aq)$ are 1 our coefficients cannot be reduced to smaller whole numbers.

Practice Exercises

4.24 | Write the balanced chemical equation that describes what happens when a solution containing calcium chloride is mixed with a solution containing potassium phosphate and the product of the reaction is solid calcium phosphate and a solution of potassium chloride. (*Hint:* Write the correct formulas based on information in Chapter 3.)

4.25 | When aqueous solutions of calcium nitrate, $Ca(NO_3)_2$, and ammonium phosphate, $(NH_4)_3PO_4$, are mixed, a reaction occurs in which solid calcium phosphate, $Ca_3(PO_4)_2$, separates from the solution. The other product is $NH_4NO_3(aq)$. Write the balanced equation.

The strategy of balancing whole units of polyatomic ions, like PO_4, as a group is extremely useful. Using this method, we have less atom counting to do and balancing equations is often easier.

Calculations that Use Balanced Chemical Equations

So far we have focused on mole ratios between elements within a single compound. We have seen that the essential conversion factor between substances within a compound is the mole ratio obtained from the compound's formula. In this section, we'll see that the same techniques can be used to relate substances involved in a chemical reaction. The tool that relates substances involved in a reaction is the mole ratio obtained from the coefficients of the balanced chemical equation.

Establishing Mole-to-Mole Ratios

To see how chemical equations can be used to obtain mole-to-mole relationships, consider the equation that describes the burning of octane (C_8H_{18}) in oxygen (O_2) to give carbon dioxide and water vapor:

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

■ The chemical equation gives the relative amounts of each of the molecules that participate in a reaction. It does not mean that 2 octane molecules actually collide with 25 O_2 molecules. The actual reaction occurs in many steps that the chemical equation does not show.

This equation can be interpreted on the molecular scale as follows:

> *When two molecules of liquid octane react with twenty-five molecules of oxygen gas, sixteen molecules of carbon dioxide gas and eighteen molecules of water vapor are produced.*

This statement immediately suggests many equivalence relationships that can be used to build conversion factors for stoichiometry problems:

TOOLS

Equivalencies from balanced chemical equations

$$2 \text{ molecules } C_8H_{18} \Leftrightarrow 25 \text{ molecules } O_2$$

$$2 \text{ molecules } C_8H_{18} \Leftrightarrow 16 \text{ molecules } CO_2$$

$$2 \text{ molecules } C_8H_{18} \Leftrightarrow 18 \text{ molecules } H_2O$$

$$25 \text{ molecules } O_2 \Leftrightarrow 16 \text{ molecules } CO_2$$

$$25 \text{ molecules } O_2 \Leftrightarrow 18 \text{ molecules } H_2O$$

$$16 \text{ molecules } CO_2 \Leftrightarrow 18 \text{ molecules } H_2O$$

Any of these *microscopic* relationships can be scaled up to the *macroscopic* laboratory scale by multiplying both sides of the equivalency by Avogadro's number, which effectively allows us to replace "molecules" with "moles" or "mol":

$$2 \text{ mol } C_8H_{18} \Leftrightarrow 25 \text{ mol } O_2$$

$$2 \text{ mol } C_8H_{18} \Leftrightarrow 16 \text{ mol } CO_2$$

$$2 \text{ mol } C_8H_{18} \Leftrightarrow 18 \text{ mol } H_2O$$

$$25 \text{ mol } O_2 \Leftrightarrow 16 \text{ mol } CO_2$$

$$25 \text{ mol } O_2 \Leftrightarrow 18 \text{ mol } H_2O$$

$$16 \text{ mol } CO_2 \Leftrightarrow 18 \text{ mol } H_2O$$

We can interpret the equation on a macroscopic (mole) scale as follows:

> *Two moles of liquid octane react with twenty-five moles of oxygen gas to produce sixteen moles of carbon dioxide gas and eighteen moles of water vapor.*

To use these equivalencies in a stoichiometry problem, the equation must be **balanced**. That means that every atom found in the reactants must also be found somewhere in the products. You must always check to see whether this is true for a given equation before you can use the coefficients to build equivalencies and conversion factors.

First, let's see how mole-to-mole relationships obtained from a chemical equation can be used to convert moles of one substance to moles of another when both substances are involved in a chemical reaction.

Example 4.15
Stoichiometry of Chemical Reactions

How many moles of sodium phosphate can be made from 0.240 mol of sodium hydroxide by the following unbalanced equation?

$$NaOH(aq) + H_3PO_4(aq) \longrightarrow Na_3PO_4(aq) + H_2O$$

■ **Analysis:** We are given an unbalanced equation and will have to balance it first before we can find an appropriate mole ratio. Then the question asks us to relate amounts, in moles, of two different substances. As in Example 4.5, all we need for this conversion is a mole ratio.

■ **Assembling the Tools:** We first balance the equation as we did previously,

$$3NaOH(aq) + H_3PO_4(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O$$

Now an equivalence derived from the coefficients of the balanced equation is written as

$$3 \text{ mol NaOH} \Leftrightarrow 1 \text{ mol } Na_3PO_4$$

This enables us to prepare the mole ratio conversion factor that we need.

■ **Solution:** We start by writing the question in equation form as

$$0.240 \text{ mol NaOH} \Leftrightarrow ? \text{ mol } Na_3PO_4$$

Using the mole ratio $\frac{1 \text{ mol } Na_3PO_4}{3 \text{ mol NaOH}}$, we convert 0.240 mol NaOH to the number of moles of Na_3PO_4:

$$0.240 \cancel{\text{mol NaOH}} \times \frac{1 \text{ mol } Na_3PO_4}{3 \cancel{\text{mol NaOH}}} = 0.0800 \text{ mol } Na_3PO_4$$

The result states that we can make 0.0800 mol Na_3PO_4 from 0.240 mol NaOH. Recall that the coefficients, 1 and 3, in the conversion factor are exact numbers, so our answer has three significant figures.

■ Is the Answer Reasonable? The balanced equation tells us that 3 mol NaOH ⇔ 1 mol Na_3PO_4, so the actual number of moles of Na_3PO_4 (0.0800 mol) should be one-third the actual number of moles of NaOH (0.240 mol), and it is. We can also check that the units cancel correctly.

Practice Exercises

4.26 | In the reaction $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$, how many moles of O_2 are needed to produce 6.76 moles of SO_3? (*Hint:* Write the equality that relates O_2 to SO_3.)

4.27 | How many moles of sulfuric acid, H_2SO_4, are needed to react with 0.366 mol of NaOH by the following balanced chemical equation?

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O$$

Mass-to-Mass Calculations

The most common stoichiometric calculation the chemist does is to relate grams of one substance with grams of another in a chemical reaction. For example, consider glucose, $C_6H_{12}O_6$, one of the body's primary energy sources. The body combines glucose and oxygen, in a process called metabolism, to give carbon dioxide and water. The balanced equation for the overall reaction is

$$C_6H_{12}O_6(aq) + 6\ O_2(aq) \longrightarrow 6\ CO_2(aq) + 6\ H_2O(l)$$

How many grams of oxygen must the body take in to completely process 1.00 g of glucose? The problem can be expressed as

$$1.00\ g\ C_6H_{12}O_6 \Leftrightarrow ?\ g\ O_2$$

The first thing we should notice about this problem is that we're relating *two different substances* in a reaction. The equality that relates the substances is the mole-to-mole relationship between glucose and O_2 given by the chemical equation. In this case, the equation tells us that 1 mol $C_6H_{12}O_6$ ⇔ 6 mol O_2. It is very important to realize that there is no direct conversion between the mass of $C_6H_{12}O_6$ and the mass of O_2. We need to convert the mass of glucose to moles of glucose, then we use the mole ratio to convert moles of glucose to moles of oxygen, and finally we convert moles of oxygen to mass of oxygen. This sequence, indicating where we use the mole-to-mole equivalence, is shown below

Mass-to-mass calculations using balanced chemical equations

$$\boxed{1\ \text{mol}\ C_6H_{12}O_6 \Leftrightarrow 6\ \text{mol}\ O_2}$$

$$1.00\ g\ C_6H_{12}O_6 \longrightarrow \text{mol}\ C_6H_{12}O_6 \longrightarrow \text{mol}\ O_2 \longrightarrow g\ O_2$$

The molar mass is used twice as a tool, once for converting 1.00 g of glucose to moles and again for converting moles of O_2 to grams of O_2.

Figure 4.4 outlines this flow for *any* stoichiometry problem that relates reactant or product masses. If we know the *balanced equation* for a reaction and the *mass* of any

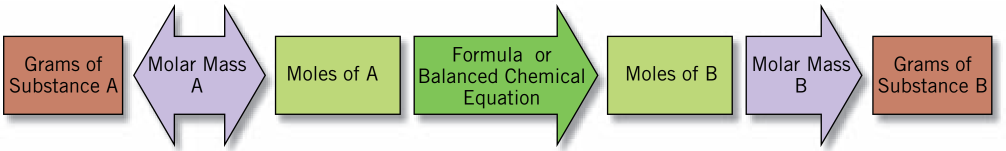


Figure 4.4 | **The sequence of calculations for solving stoichiometry problems.** This sequence applies to all calculations that start with the mass of one substance *A* and require the mass of a second substance *B* as the answer. Each box represents a measured or calculated quantity. Each arrow represents one of our chemical tools.

reactant or product, we can calculate the required or expected mass of *any* other substance in the equation. Example 4.16 shows how it works.

Example 4.16
Stoichiometric Mass Calculations

Portland cement is a mixture of the oxides of calcium, aluminum, and silicon. The raw material for its calcium oxide is calcium carbonate, which occurs as the chief component of a natural rock, limestone. When calcium carbonate is strongly heated it decomposes. One product, carbon dioxide, is driven off to leave the desired calcium oxide as the only other product.

A chemistry student is to prepare 1.50×10^2 g of calcium oxide in order to test a particular "recipe" for Portland cement. How many grams of calcium carbonate should be used, assuming 100% conversion to product?

■ **Analysis:** As usual, this is a multi-part problem. First, we need to determine the formulas of the compounds and then write a balanced chemical reaction. Then we will perform the conversions from the given 1.50×10^2 grams of calcium oxide to moles of calcium oxide, then to moles of calcium carbonate, and then to grams of calcium carbonate.

■ **Assembling the Tools:** We need the nomenclature tools in Chapter 3 to translate the names of the compounds to formulas and then write the balanced chemical equation, which is

$$\text{CaCO}_3(s) \xrightarrow{\text{heat}} \text{CaO}(s) + \text{CO}_2(g)$$

■ Special reaction conditions are often shown with words or symbols above the arrow. In this reaction, temperatures above 2000 °C are needed and this is indicated with the word, heat, above the arrow.

Now we can write our sequence of conversions using formulas,

$$1.50 \times 10^2 \text{ g CaO} \longrightarrow \text{mol CaO} \longrightarrow \text{mol CaCO}_3 \longrightarrow \text{g CaCO}_3$$

We need tools for converting the mass to moles for CaO in the first step and the mass to moles for CaCO_3 in the last step. They are

$$56.08 \text{ g CaO} = 1 \text{ mol CaO} \quad \text{and} \quad 1 \text{ mol CaCO}_3 = 100.09 \text{ g CaCO}_3$$

Finally, we need a tool for the mole-to-mole conversion. Using our balanced chemical equation, the equivalence is

$$1 \text{ mol CaO} \Leftrightarrow 1 \text{ mol CaCO}_3$$

■ **Solution:** We start by writing the question as an equation.

$$1.50 \times 10^2 \text{ g CaO} \Leftrightarrow ? \text{ g CaCO}_3$$

Reviewing our sequence of calculation we can write the sequence of steps indicating where we use each of our tools.

$$1.50 \times 10^2 \text{ g CaO} \xrightarrow[\boxed{56.08 \text{ g CaO} = 1 \text{ mol CaO}}]{} \text{mol CaO} \xrightarrow{\boxed{1 \text{ mol CaO} \Leftrightarrow 1 \text{ mol CaCO}_3}} \text{mol CaCO}_3 \xrightarrow[\boxed{1 \text{ mol CaCO}_3 = 100.09 \text{ g CaCO}_3}]{} \text{g CaCO}_3$$

Starting from the left, we assemble conversion factors so the units cancel correctly:

$$1.50 \times 10^2 \ \cancel{\text{g CaO}} \times \left(\frac{1 \ \cancel{\text{mol CaO}}}{56.08 \ \cancel{\text{g CaO}}}\right) \times \left(\frac{1 \ \cancel{\text{mol CaCO}_3}}{1 \ \cancel{\text{mol CaO}}}\right) \times \left(\frac{100.09 \text{ g CaCO}_3}{1 \ \cancel{\text{mol CaCO}_3}}\right) = 268 \text{ g CaCO}_3$$

Notice how the calculation flows from grams of CaO to moles of CaO, then to moles of $CaCO_3$ (using the equation), and finally to grams of $CaCO_3$. We cannot emphasize too much that *the key step in all calculations of reaction stoichiometry is the use of the balanced equation.*

■ This 5 to 1/5 range for conversions of the mass of A to a mass of B holds true for most (maybe 90–95%) calculations. If your answer is outside this range, do a very careful check for errors.

■ **Is the Answer Reasonable?** In a mass-to-mass calculation like this, the first check is the magnitude of the answer compared to the starting mass. In the majority of reactions the calculated mass is not less than $\frac{1}{5}$ of the starting mass nor is it larger than five times the starting mass. Our result is reasonable based on this criteria. We can make a more detailed check by first checking that the units cancel properly. We can also round to one or two significant figures and estimate the answer. We would estimate $\frac{150 \times 100}{50} = 300$, and this value is close to our answer of 268, giving us confidence that the answer is reasonable.

Example 4.17
Stoichiometric Mass Calculations

Figure 4.5 | **The thermite reaction.** Pictured here is a device for making white-hot iron by the reaction of aluminum with iron oxide and letting the molten iron run down into a mold between ends of two steel railroad rails. This welds the rails together. *(Wikimedia Commons)*

The thermite reaction is one of the most spectacular reactions with flames, sparks and glowing molten iron. Here aluminum reacts with iron(III) oxide to produce aluminum oxide and metallic iron. So much heat is generated that the iron forms in the liquid state (Figure 4.5).

A certain welding operation requires at least 86.0 g of iron each time a weld is made. What is the minimum mass, in grams, of iron(III) oxide that must be used for each weld? Also calculate how many grams of aluminum are needed.

■ **Analysis:** First, we need to determine the formulas of the compounds so we can write a balanced chemical equation. Next, we need to convert the 86.0 g Fe to the needed mass of iron(III) oxide. Remember that all problems in reaction stoichiometry must be solved at the mole level because an equation's coefficients disclose *mole* ratios, not mass ratios. The sequence of conversions to use is

$$\text{86.0 g iron} \longrightarrow \text{mol iron} \longrightarrow \text{mol iron(III) oxide} \longrightarrow \text{g iron(III) oxide}$$

For the second calculation we calculate the number of grams of Al needed, but we know that we must first find the number of *moles* of Al required. For this second calculation the sequence is

$$\text{86.0 g iron} \longrightarrow \text{mol iron} \longrightarrow \text{mol aluminum} \longrightarrow \text{g aluminum}$$

■ **Assembling the Tools:** We use our nomenclature tools from Chapter 3 to determine that Al and Fe_2O_3 are the reactants and that Fe and Al_2O_3 are the products. The balanced equation is:

$$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(l)$$

The following conversion equalities are needed to calculate the mass of Fe_2O_3

$$55.85 \text{ g Fe} = 1 \text{ mol Fe}$$
$$1 \text{ mol } Fe_2O_3 \Leftrightarrow 2 \text{ mol Fe}$$
$$159.70 \text{ g } Fe_2O_3 = 1 \text{ mol } Fe_2O_3$$

Next, we need the following conversion equalities to calculate the mass of aluminum:

$$55.85 \text{ g Fe} = 1 \text{ mol Fe}$$
$$2 \text{ mol Al} \Leftrightarrow 2 \text{ mol Fe}$$
$$26.98 \text{ g Al} = 1 \text{ mol Al}$$

Solution: Now we state the first part of the problem in mathematical form:

$$86.0\ \text{g Fe} \Leftrightarrow ?\ \text{g Fe}_2\text{O}_3$$

We'll set up the first calculation as a chain. The steps are summarized below each conversion factor.

$$86.0\ \cancel{\text{g Fe}} \times \frac{1\ \cancel{\text{mol Fe}}}{55.85\ \cancel{\text{g Fe}}} \times \frac{1\ \cancel{\text{mol Fe}_2\text{O}_3}}{2\ \cancel{\text{mol Fe}}} \times \frac{159.70\ \text{g Fe}_2\text{O}_3}{1\ \cancel{\text{mol Fe}_2\text{O}_3}} = 123\ \text{g Fe}_2\text{O}_3$$

$$\text{grams Fe} \longrightarrow \text{moles Fe} \longrightarrow \text{moles Fe}_2\text{O}_3 \longrightarrow \text{grams Fe}_2\text{O}_3$$

A minimum of 123 g of Fe_2O_3 is required to make 86.0 g of Fe.

To calculate the mass of aluminum, we follow a similar sequence, using the conversion factors in order so that the units cancel as shown. We employ another chain calculation to find the mass of Al needed to make 86.0 g of Fe.

We could simplify the mole ratio to 1 mol Al ⇔ 1 mol Fe. Leaving the 2-to-2 ratio maintains the connection to the coefficients in the balanced equation.

$$86.0\ \cancel{\text{g Fe}} \times \frac{1\ \cancel{\text{mol Fe}}}{55.85\ \cancel{\text{g Fe}}} \times \frac{2\ \cancel{\text{mol Al}}}{2\ \cancel{\text{mol Fe}}} \times \frac{26.98\ \text{g Al}}{1\ \cancel{\text{mol Al}}} = 41.5\ \text{g Al}$$

$$\text{grams Fe} \longrightarrow \text{moles Fe} \longrightarrow \text{moles Al} \longrightarrow \text{grams Al}$$

Are the Answers Reasonable? The estimate that our answers in a mass-to-mass calculation should be within 1/5 to 5 times the initial mass is true for both Al and Fe_2O_3. Rounding the numbers to one significant figure and estimating the answer (after rechecking that the units cancel properly) results in

$$\frac{90 \times 200}{60 \times 2} = 150\ \text{g Fe}_2\text{O}_3 \quad \text{and} \quad \frac{90 \times 30}{60} = 45\ \text{g Al}$$

Both estimates are close to our calculated values and give confidence that our answers are reasonable.

Practice Exercises

4.28 | Using the information in Example 4.17, calculate the mass of Al_2O_3 formed under the conditions specified. (*Hint:* Recall the law of conservation of mass.)

4.29 | How many grams of carbon dioxide are also produced by the reaction described in Example 4.16?

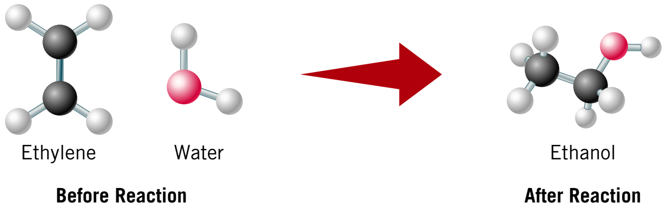
4.5 | Limiting Reactants

Limiting Reactants Viewed at the Molecular Level

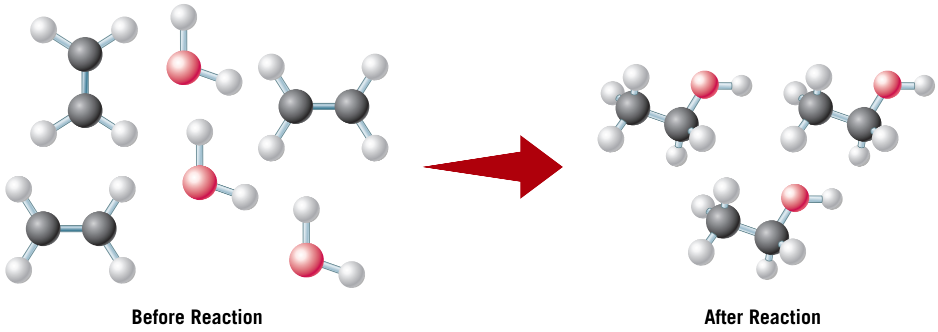
We've seen that balanced chemical equations can tell us how to mix reactants together in just the right proportions to get a certain amount of product. For example, ethanol, C_2H_5OH, is prepared industrially as follows:

$$\underset{\text{ethylene}}{\text{C}_2\text{H}_4} + \text{H}_2\text{O} \longrightarrow \underset{\text{ethanol}}{\text{C}_2\text{H}_5\text{OH}}$$

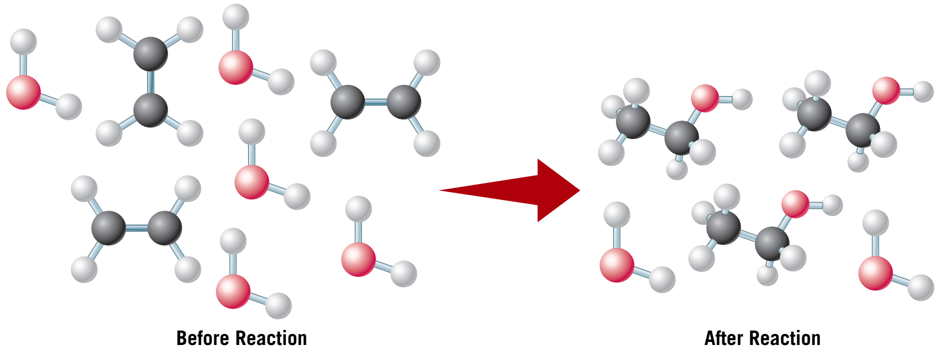
We often interpret the equation on a laboratory scale using moles. Every mole of ethylene that reacts requires one mole of water to produce one mole of ethanol. Let's look at this reaction at the molecular level. Now the equation tells us that one molecule of ethylene will react with one molecule of water to give one molecule of ethanol.



If we have three molecules of ethylene reacting with three molecules of water, then three ethanol molecules are produced:



What happens if we mix three molecules of ethylene with five molecules of water? The ethylene will be completely used up before all the water is, and the product will contain two unreacted water molecules:



■ Notice that in both the "before" and "after" views of the reaction, the numbers of carbon, hydrogen, and oxygen atoms are the same.

We don't have enough ethylene to use up all the water. The excess water remains after the reaction stops. This situation can be a problem in the manufacture of chemicals because not only do we waste one of our reactants (water, in this case), but we also obtain a product that is contaminated with unused reactant.

In this reaction mixture, ethylene is called the **limiting reactant** because it limits the amount of product (ethanol) that forms. The water is called an **excess reactant,** because we have more of it than is needed to completely consume all the ethylene.

To predict the amount of product we'll actually obtain in a reaction, we need to know which of the reactants is the limiting reactant. In the example above, we saw that we needed only 3 H_2O molecules to react with 3 C_2H_4 molecules, but we had 5 H_2O molecules, so H_2O is present in excess and C_2H_4 is the limiting reactant. We could also have reasoned that 5 molecules of H_2O would require 5 molecules of C_2H_4, and since we have only 3 molecules of C_2H_4, it must be the limiting reactant.

A Strategy for Solving Limiting Reactant Problems

At the start of this chapter we referred to the billions of hamburger buns produced each year to reflect the large number of atoms and molecules we work with. Construction of hamburgers can also be a limiting reactant problem. For instance, how many quarter-pound hamburgers can be made from a package of eight hamburger rolls, a pound of hamburger meat, a bottle of ketchup, and a bottle of pickles? We can quickly see that one pound of hamburger meat will make four quarter-pound hamburgers. We obviously have an excess of buns, catsup, and pickles. The hamburger meat is our limiting reactant, and four hamburgers is the most we can prepare.

As we saw above, there are several steps involved in solving limiting reactant problems. First, we identify a limiting reactant problem by the fact that the amount of more than one reactant is given. Next, we need to identify the limiting reactant, and finally we solve the problem based on the amount of limiting reactant at hand. The first step is easy. Next, when finding the limiting reactant, we arbitrarily pick one of the reactants and calculate how much of the second reactant is needed. If the amount calculated for the second reactant is less than what is given, there is an excess of the second reactant and therefore the first reactant is limiting. If the calculated amount of the second reactant is more than what was given, then it will be consumed first and the second reactant is limiting.

TOOLS

Limiting reactant calculations

Once we have identified the limiting reactant, it is possible to compute the amount of product that will actually form and the amount of excess reactant that will be left over after the reaction stops. For the final calculations we must use the amount of the limiting reactant given in the statement of the problem.

Example 4.18 shows how to solve a typical limiting reactant problem when the amounts of the reactants are given in mass units.

Example 4.18
Limiting Reactant Calculation

Gold(III) hydroxide is used for electroplating gold onto other metals. It can be made by the following reaction.

$$2KAuCl_4(aq) + 3Na_2CO_3(aq) + 3H_2O \longrightarrow 2Au(OH)_3(aq) + 6NaCl(aq) + 2KCl(aq) + 3CO_2(g)$$

To prepare a fresh supply of $Au(OH)_3$, a chemist at an electroplating plant has mixed 20.00 g of $KAuCl_4$ with 25.00 g of Na_2CO_3 (both dissolved in a large excess of water). What is the maximum number of grams of $Au(OH)_3$ that can form?

■ **Analysis:** The clue that tells us this is a limiting reactant question is that *the quantities of two reactants are given*. Now we will break this question into two separate steps, identifying the limiting reactant and then calculating the grams of $Au(OH)_3$ produced.

Step I: To identify the limiting reactant, we arbitrarily pick one of the reactants ($KAuCl_4$ or Na_2CO_3; we were told that water is in excess, so we know that it does not limit the reaction) and calculate how much of the second reactant is needed. Based on the result we will be able to decide which reactant is limiting. We will need to use a combination of our stoichiometry tools to solve this problem.

Step II: Once we've identified the limiting reactant we can use it to calculate the amount of $Au(OH)_3$ produced using the following sequence of conversions. Notice that this sequence is essentially the same as the one we used in Figure 4.4.

$$\text{g limiting reactant} \longrightarrow \text{mol limiting reactant} \longrightarrow \text{mol } Au(OH)_3 \longrightarrow \text{g } Au(OH)_3$$

■ **Assembling the Tools—Step I:** Our tool for limiting reactant calculations outlines the process for identifying the limiting reactant. First, we calculate the amount of reactant 1 that will react with reactant 2. To do this we use the following sequence of calculations:

$$\text{mass of reactant 1} \longrightarrow \text{mol reactant 1} \longrightarrow \text{mol reactant 2} \longrightarrow \text{mass reactant 2}$$

This is our typical mass-to-mass calculation that requires the following relationships

$$1 \text{ mol KAuCl}_4 = 377.88 \text{ g KAuCl}_4$$

$$2 \text{ mol KAuCl}_4 \Leftrightarrow 3 \text{ mol Na}_2\text{CO}_3$$

$$1 \text{ mol Na}_2\text{CO}_3 = 105.99 \text{ g Na}_2\text{CO}_3$$

■ **Solution—Step I:** We will show, in the two calculations that follow, the process used to identify the limiting reactant. In solving a limiting reactant problem you will need to do only one of these calculations.

We start with KAuCl_4 as the reactant to work with and calculate how many grams of Na_2CO_3 *should* be provided to react with 20.00 g of KAuCl_4. We'll set up a chain calculation as follows.

$$\text{grams KAuCl}_4 \longrightarrow \text{moles KAuCl}_4 \longrightarrow \text{moles Na}_2\text{CO}_3 \longrightarrow \text{grams Na}_2\text{CO}_3$$

$$20.00 \text{ g } \cancel{\text{KAuCl}_4} \times \frac{1 \text{ mol } \cancel{\text{KAuCl}_4}}{377.88 \text{ g } \cancel{\text{KAuCl}_4}} \times \frac{3 \cancel{\text{ mol Na}_2\text{CO}_3}}{2 \cancel{\text{ mol KAuCl}_4}} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{1 \cancel{\text{ mol Na}_2\text{CO}_3}} = 8.415 \text{ g Na}_2\text{CO}_3$$

We find that 20.00 g of KAuCl_4 needs of Na_2CO_3. The given amount of 25.00 g of Na_2CO_3 is more than enough to let the KAuCl_4 react completely. *We conclude that KAuCl_4 is the limiting reactant and that Na_2CO_3 is present in excess.*

We start with Na_2CO_3 as the reactant to work with and calculate how many grams of KAuCl_4 *should* be provided to react with 25.00 g of Na_2CO_3. Again we perform a chain calculation using the appropriate conversion factors

$$\text{grams Na}_2\text{CO}_3 \longrightarrow \text{moles Na}_2\text{CO}_3 \longrightarrow \text{moles KAuCl}_4 \longrightarrow \text{grams KAuCl}_4$$

$$25.00 \text{ g } \cancel{\text{Na}_2\text{CO}_3} \times \frac{1 \text{ mol } \cancel{\text{Na}_2\text{CO}_3}}{105.99 \text{ g } \cancel{\text{Na}_2\text{CO}_3}} \times \frac{2 \cancel{\text{ mol KAuCl}_4}}{3 \cancel{\text{ mol Na}_2\text{CO}_3}} \times \frac{377.88 \text{ g KAuCl}_4}{1 \cancel{\text{ mol KAuCl}_4}} = 59.42 \text{ g KAuCl}_4$$

We find that 25.00 g Na_2CO_3 would require almost three times the mass of KAuCl_4 provided, so *we again conclude that KAuCl_4 is the limiting reactant.*

The result from either calculation above is sufficient to designate KAuCl_4 as the limiting reactant. Now we proceed to Step II.

■ After identifying the limiting reactant, return to the statement of the problem and use the amount of the limiting reactant given in the problem to perform further calculations.

■ **Assembling the Tools—Step II:** Since KAuCl_4 is the limiting reactant, we can calculate the mass of Au(OH)_3 using the sequence of steps

$$\text{mass of KAuCl}_4 \longrightarrow \text{moles of KAuCl}_4 \longrightarrow \text{moles of Au(OH)}_3 \longrightarrow \text{mass of Au(OH)}_3$$

Now we write the equalities we need to finish the problem:

$$1 \text{ mol KAuCl}_4 = 377.88 \text{ g KAuCl}_4$$

$$2 \text{ mol KAuCl}_4 \Leftrightarrow 2 \text{ mol Au(OH)}_3$$

$$1 \text{ mol Au(OH)}_3 = 247.99 \text{ g Au(OH)}_3$$

■ **Solution—Step II:** From here on, we have a routine calculation converting the mass of the limiting reactant, KAuCl_4, to the mass of product, Au(OH)_3. We set up the following chain calculation.

$$\text{grams KAuCl}_4 \longrightarrow \text{moles KAuCl}_4 \longrightarrow \text{moles Au(OH)}_3 \longrightarrow \text{grams Au(OH)}_3$$

$$20.00\ \cancel{\text{g KAuCl}_4} \times \left(\frac{1\ \cancel{\text{mol KAuCl}_4}}{377.88\ \cancel{\text{g KAuCl}_4}}\right) \times \left(\frac{2\ \cancel{\text{mol Au(OH)}_3}}{2\ \cancel{\text{mol KAuCl}_4}}\right) \times \left(\frac{247.99\ \text{g Au(OH)}_3}{1\ \cancel{\text{mol Au(OH)}_3}}\right) = 13.13\ \text{g Au(OH)}_3$$

Thus from 20.00 g of $KAuCl_4$ we can make a maximum of 13.13 g of $Au(OH)_3$.

In this synthesis, some of the initial 25.00 g of Na_2CO_3 is left over. Since one of our calculations showed that 20.00 g of $KAuCl_4$ requires only 8.415 g of Na_2CO_3 out of 25.00 g Na_2CO_3, the difference, (25.00 g − 8.415 g) = 16.58 g of Na_2CO_3, remains unreacted. It is possible that the chemist used an excess to ensure that every last bit of the very expensive $KAuCl_4$ would be changed to $Au(OH)_3$.

Notice that by breaking this problem into two parts, we were able to solve two mass-to-mass calculations to get the answer we needed.

Are the Answers Reasonable? First, the resulting masses are within the range of $\frac{1}{5}$ to 5 times the starting mass and are not unreasonable. Again, we check that our units cancel properly and then we estimate the answer as $\frac{20 \times 200}{400} = 10$ g $Au(OH)_3$, which is close enough to our answer to give confidence that the calculation was done correctly.

Practice Exercises

4.30 | The reaction between the limestone and hydrochloric acid produces carbon dioxide as shown in the reaction.

$$CaCO_3(s) + 2HCl\,(aq) \longrightarrow CO_2(g) + CaCl_2(aq) + H_2O$$

How many grams of CO_2 can be made by reacting 125 g of $CaCO_3$ with 125 g of HCl? How many grams of which reactant are left over? (*Hint:* Find the limiting reactant.)

4.31 | In an industrial process for making nitric acid, the first step is the reaction of ammonia with oxygen at high temperature in the presence of a platinum gauze. Nitrogen monoxide forms as follows.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

How many grams of nitrogen monoxide can form if a mixture initially contains 30.00 g of NH_3 and 40.00 g of O_2?

4.6 | Theoretical Yield and Percentage Yield

In most experiments designed for chemical synthesis, the amount of a product actually isolated falls short of the calculated maximum amount. Losses occur for several reasons. Some are mechanical, such as materials sticking to glassware. In some reactions, losses occur by the evaporation of a volatile product. In others, a product is a solid that separates from the solution as it forms because it is largely insoluble. The solid is removed by filtration. What stays in solution, although relatively small, contributes to some loss of product.

One of the common causes of obtaining less than the stoichiometric amount of a product is the occurrence of a **competing reaction**. It produces a **by product**, a substance made by a reaction that competes with the **main reaction**. The synthesis of phosphorus trichloride, for example, gives some phosphorus pentachloride as well, because PCl_3 can react further with Cl_2.

$$\begin{aligned} &\text{Main reaction:} && 2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l) \\ &\text{Competing reaction:} && PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s) \end{aligned}$$

The competition is between newly formed PCl_3 and still unreacted phosphorus for still unchanged chlorine.

When determining the percentage yield, you must be given the actual yield of the experiment; it cannot be calculated.

TOOLS

Theoretical, actual, and percentage yields

The **actual yield** of desired product is simply how much is isolated, stated in either mass units or moles. The **theoretical yield** of the product is what must be obtained if no losses occur. When less than the theoretical yield of product is obtained, chemists generally calculate the *percentage yield* of product to describe how well the preparation went. The **percentage yield** is the actual yield calculated as a percentage of the theoretical yield.

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{4.2}$$

Both the actual and theoretical yields must be in the same units.

It is important to realize that the actual yield is an experimentally determined quantity. It cannot be calculated. The theoretical yield is always a calculated quantity based on a chemical equation and the amounts of the reactants available.

Let's now work an example that combines the determination of the limiting reactant with a calculation of percentage yield.

Example 4.19
Calculating a Percentage Yield

A chemist set up a synthesis of phosphorus trichloride by mixing 12.0 g of phosphorus with 35.0 g chlorine gas and obtained 42.4 g of solid phosphorus trichloride. Calculate the percentage yield of this compound.

Analysis: We start by determining the formulas for the reactants and products and then balancing the chemical equation. Phosphorus is represented as P(*s*) and chlorine gas is $Cl_2(g)$ and the product is $PCl_3(s)$. The balanced equation is

$$2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(s)$$

Now we notice that the masses of *both* reactants are given, so this must be a limiting reactant problem. The first step is to figure out which reactant, P or Cl_2, is the limiting reactant, because we must base all calculations on the limiting reactant. When we know the limiting reactant, we can calculate the theoretical yield of product, $PCl_3(s)$. Finally we calculate the percentage yield. The three main steps are summarized as,

$$\begin{array}{c}\text{Determine the}\\ \text{limiting reactant}\end{array} \longrightarrow \begin{array}{c}\text{Determine the}\\ \text{theoretical yield}\end{array} \longrightarrow \begin{array}{c}\text{Calculate the}\\ \text{percentage yield}\end{array}$$

Assembling the Tools: To solve the first two steps, our basic tools are the relationships

$$1 \text{ mol P} = 30.97 \text{ g P}$$
$$1 \text{ mol } Cl_2 = 70.90 \text{ g } Cl_2$$
$$3 \text{ mol } Cl_2 \Leftrightarrow 2 \text{ mol P}$$

For the percentage yield our tool is Equation 4.2.

Solution: In any limiting reactant problem, we can arbitrarily pick one reactant and do a calculation to see whether it can be entirely used up. We'll choose phosphorus and see whether there is enough to react with 35.0 g of chlorine. The following calculation gives us the answer.

$$12.0 \ \cancel{\text{g P}} \times \frac{1 \ \cancel{\text{mol P}}}{30.97 \ \cancel{\text{g P}}} \times \frac{3 \ \cancel{\text{mol } Cl_2}}{2 \ \cancel{\text{mol P}}} \times \frac{70.90 \text{ g } Cl_2}{1 \ \cancel{\text{mol } Cl_2}} = 41.2 \text{ g } Cl_2$$

Thus, with 35.0 g of Cl_2 provided but 41.2 g of Cl_2 needed, there is not enough Cl_2 to react with all 12.0 g of P. The Cl_2 will be all used up before the P is used up, so Cl_2 is the limiting reactant. We therefore base the calculation of the theoretical yield of PCl_3 on Cl_2.

(We must be careful to use the 35.0 g of Cl_2 given in the problem, *not* the 41.2 g calculated while we determined the limiting reactant.)

To find the *theoretical yield* of PCl_3, we calculate how many grams of PCl_3 could be made from 35.0 g of Cl_2 if everything went perfectly according to the equation given.

$$35.0\ \cancel{\text{g Cl}_2} \times \frac{1\ \cancel{\text{mol Cl}_2}}{70.90\ \cancel{\text{g Cl}_2}} \times \frac{2\ \cancel{\text{mol PCl}_3}}{3\ \cancel{\text{mol Cl}_2}} \times \frac{137.32\ \text{g PCl}_3}{1\ \cancel{\text{mol PCl}_3}} = 45.2\ \text{g PCl}_3$$

$$\text{grams Cl}_2 \longrightarrow \text{moles Cl}_2 \longrightarrow \text{moles PCl}_3 \longrightarrow \text{grams PCl}_3$$

The actual yield was 42.4 g of PCl_3, not 45.2 g, so the percentage yield is calculated as follows.

$$\text{Percentage yield} = \frac{42.4\ \text{g PCl}_3}{45.2\ \text{g PCl}_3} \times 100\% = 93.8\%$$

Thus 93.8% of the theoretical yield of PCl_3 was obtained.

■ **Is the Answer Reasonable?** The obvious check is that the calculated or theoretical yield can never be *less* than the actual yield. Second, our theoretical yield is within the range of 1/5 to 5 times the starting amount. Finally, one way to estimate the theoretical yield, after checking that all units cancel properly, is

$$\frac{40 \times 2 \times 100}{70 \times 3} = \frac{80 \times 100}{210} \approx \frac{80}{2} \approx 40\ \text{g PCl}_3$$

which is close to the 45.2 g PCl_3 we calculated.

Practice Exercises

4.32 | In the synthesis of aspirin we react salicylic acid with acetic anhydride. The balanced chemical equation is:

$$\underset{\text{salicylic acid}}{2\text{HOOCC}_6\text{H}_4\text{OH}} + \underset{\text{acetic anhydride}}{\text{C}_4\text{H}_6\text{O}_3} \longrightarrow \underset{\text{acetyl salicylic acid}}{2\text{HOOCC}_6\text{H}_4\text{O}_2\text{C}_2\text{H}_3} + \underset{\text{water}}{\text{H}_2\text{O}}$$

If we mix together 28.2 grams of salicylic acid with 15.6 grams of acetic anhydride in this reaction, we obtain 30.7 grams of aspirin. What are the theoretical and percentage yields of our experiment? (*Hint:* What is the limiting reactant?)

4.33 | Ethanol, C_2H_5OH, can be converted to acetic acid (the acid in vinegar), $HC_2H_3O_2$, by the action of sodium dichromate in aqueous sulfuric acid according to the following equation.

$$\begin{aligned}&3\text{C}_2\text{H}_5\text{OH}(aq) + 2\text{Na}_2\text{Cr}_2\text{O}_7(aq) + 8\text{H}_2\text{SO}_4(aq) \longrightarrow \\ &\qquad 3\text{HC}_2\text{H}_3\text{O}_2(aq) + 2\text{Cr}_2(\text{SO}_4)_3(aq) + 2\text{Na}_2\text{SO}_4(aq) + 11\text{H}_2\text{O}\end{aligned}$$

In one experiment, 24.0 g of C_2H_5OH, 90.0 g of $Na_2Cr_2O_7$, and an excess of sulfuric acid were mixed, and 26.6 g of acetic acid ($HC_2H_3O_2$) was isolated. Calculate the theoretical and percentage yields of $HC_2H_3O_2$.

Multi-Step Reactions

Many chemical synthesis reactions involve more than one step to produce a product. Sometimes there can be more than ten separate reactions from the initial reactants to the final products. In such reactions, the product of one reaction is the reactant for the next. As a result, the overall percentage yield is the product of the percentage yields for all the steps along the way. The following equation is used to calculate percent yields for multi-step syntheses.

TOOLS

Multi-step percentage yield

$$\boxed{\text{Overall \% yield} = \left(\frac{\%\ \text{yield}_1}{100} \times \frac{\%\ \text{yield}_2}{100} \times \cdots\right)100\%}$$

Practice Exercise

4.34 | In producing a certain drug, one synthetic route involves three steps with percentage yields of 87.2%, 91.1%, and 86.3%. An alternate synthesis uses two steps with percentage yields of 85.5% and 84.3%. Based on the overall percent yield, which is the preferred synthesis?

Summary

Mole Concept, Avogadro's Number, and the Laboratory Scale. In the SI definition, one mole of any substance is an amount with the same number, 6.022×10^{23}, of atoms, molecules, or formula units as there are atoms in 12 g (exactly) of carbon-12. **Avogadro's number** is the title given to the number 6.022×10^{23}. Chemical equations show how atoms and molecules react (the molecular scale), whereas the **mole concept** uses the same equations in terms of moles of atoms and moles of molecules. Moles of substances have masses that are convenient for **laboratory scale** experiments.

Atomic, Molecular, and Formula Mass. Atomic masses listed on the periodic table are relative to an atomic mass of 12 (exactly) for C-12. The atomic mass of one mole of a monatomic element is often called the **gram atomic mass**. The mass of a mole of molecules is equal to the sum of the atomic masses of all the atoms in the formula and is called the **gram molecular mass**. Similarly, the mass of a mole of an ionic substance is equal to the masses of all the atoms in the ionic formula and is called the **gram formula mass**.

Molar Mass. This is a general term that may be used in place of the gram atomic mass, gram molecular mass, or gram formula mass. The **molar mass** is a tool for grams-to-moles or moles-to-grams conversions.

Empirical Formulas. An empirical formula gives the smallest whole-number ratio of the atoms in a substance. Empirical formulas may be calculated if we know the mass or percentage of each element in the compound.

Chemical Formulas. The actual composition of a molecule is given by its **molecular formula**. An **empirical formula** is generally the *only* formula we write for ionic compounds. In the case of a molecular compound, the molecular mass is a small whole-number multiple of the empirical formula mass.

Formula Stoichiometry. A chemical formula is a tool for stoichiometric calculations, because its subscripts tell us the mole ratios in which the various elements are combined.

Balanced Equations and Reaction Stoichiometry. A balanced equation is a tool for reaction stoichiometry because its coefficients disclose the stoichiometric equivalencies. When balancing an equation, only the coefficients can be adjusted, never the subscripts. All problems of reaction stoichiometry must be solved by first converting to moles.

Yields of Products. A reactant taken in a quantity less than required by another reactant, as determined by the reaction's stoichiometry, is called the **limiting reactant.** The **theoretical yield** of a product can be no more than permitted by the limiting reactant. Sometimes **competing reactions** (side reactions) producing by-products reduce the **actual yield**. The ratio of the actual to the theoretical yields, expressed as a percentage, is the **percentage yield**.

Stoichiometric Calculations. These are generally problems in which units are converted in a logical sequence of steps (see Figure 4.6). Conversion factors used in these calculations are found in the molar mass, Avogadro's number, the chemical formula, or the balanced chemical reaction.

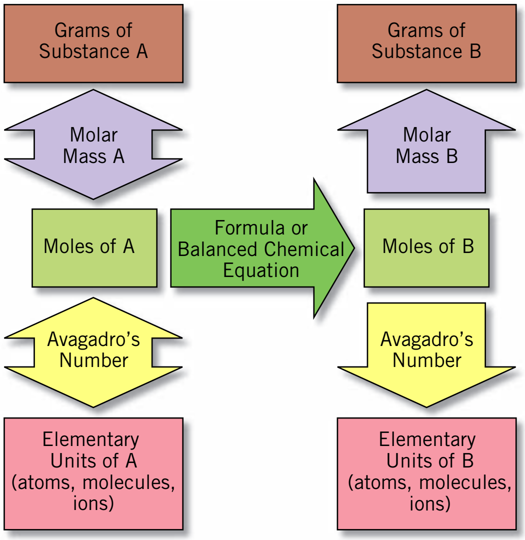

Grams of Substance A
Grams of Substance B
Molar Mass A
Molar Mass B
Moles of A
Formula or Balanced Chemical Equation
Moles of B
Avagadro's Number
Avagadro's Number
Elementary Units of A (atoms, molecules, ions)
Elementary Units of B (atoms, molecules, ions)

Figure 4.6 | **Stoichiometry pathways.** This diagram summarizes all of the possible stoichiometric calculations encountered in this chapter. The boxes represent the units that we start with and want to end at. Arrows between the boxes indicate the tools that provide the needed conversion factors.

TOOLS

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Atomic mass (page 108)
Used to form a conversion factor to calculate mass from moles of an element or moles from the mass of an element.

$$\text{Gram atomic mass of } X = \text{molar mass of } X = 1 \text{ mole } X$$

Formula mass; molecular mass (page 108)
Used to form a conversion factor to calculate mass from moles of a compound or moles from the mass of a compound.

$$\text{Gram molecular mass of } X = \text{molar mass of } X = 1 \text{ mole } X$$
$$\text{Gram formula mass of } X = \text{molar mass of } X = 1 \text{ mole } X$$

Molar Mass (page 108)
This is a general term encompassing atomic, molecular, and formula masses. All are the sum of the masses of the elements in a chemical formula.

$$\text{Molar mass of } X = 1 \text{ mole of } X$$

Avogadro's number (page 110)
It relates macroscopic lab-sized quantities (e.g., moles) to numbers of individual atomic-sized particles such as atoms, molecules, or ions.

$$1 \text{ mole } X = 6.02 \times 10^{23} \text{ particles of } X$$

Mole ratios (page 111)
Subscripts in a formula establish atom ratios and mole ratios between the elements in the substance.

Mass-to-mass conversions using formulas (page 114)
These steps are required for a mass-to-mass conversion problem using a chemical formula; also see Figure 4.6.

Percentage composition (page 116)
This describes the composition of a compound and can be the basis for computing the empirical formula. Comparing experimental and theoretical percentage compositions can help establish the identity of a compound.

$$\text{Percent of } X = \frac{\text{mass of } X \text{ in the sample}}{\text{mass of the entire sample}} \times 100\%$$

Empirical formula (page 119)
The empirical formula expresses the simplest ratio of the atoms of each element in a compound.

Determination of integer subscripts (page 121)
When determining an empirical formula, dividing all molar amounts by the smallest value often normalizes subscripts to integers. If decimals remain, multiplication by a small whole number can result in integer subscripts.

Empirical formulas from percentage composition (page 122)
Analysis of a substance often requires more than one procedure. Percentage composition (see above) helps correlate information from these different experiments, particularly when each method used may require a different mass of sample.

Balancing chemical equations (page 129)
Balancing equations involves writing the unbalanced equation and then adjusting the coefficients to get equal numbers of each kind of atom on both sides of the arrow.

Equivalencies obtained from balanced equations (page 130)

The coefficients in balanced chemical equations give us relationships between all reactants and products that can be used in factor-label calculations.

Mass-to-mass calculations using balanced equations (page 132)

A logical sequence of conversions allows calculation of all components of a chemical reaction. See Figure 4.6.

Limiting reactant calculations (page 137)

When the amount of at least two reactants is known, stoichiometry questions are answered by identifying the limiting reactant and then using the given amount of the limiting reactant to perform the required conversions.

Theoretical, actual, and percentage yields (page 140)

The theoretical yield is calculated from the limiting reactant whether stated, implied, or calculated. The actual yield must be determined by experiment, and the percentage yield relates the magnitude of the actual yield to the percentage yield.

$$\text{Percentage yield} = \frac{\text{actual mass by experiment}}{\text{theoretical mass by calculation}} \times 100\%$$

Multi-step percentage yield (page 141)

Modern chemical synthesis often involves more than one distinct reaction or step. The overall percentage yield of a multi-step synthesis is

$$\text{Overall percentage yield} = \left(\frac{\text{actual yield}_1}{\text{theoretical yield}_1} \times \frac{\text{actual yield}_2}{\text{theoretical yield}_2} \times \cdots\right)100\%$$

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Mole Concept

4.1 Using atomic mass units, how would you estimate the number of atoms in a gram of iron?

4.2 What is the definition of the mole?

4.3 Why are moles used, when all stoichiometry problems could be done using only atomic mass units?

4.4 Which contains more molecules: 2.5 mol of H_2O or 2.5 mol of H_2? Which contains more atoms? Which weighs more?

Chemical Formulas

4.5 How many moles of iron atoms are in one mole of Fe_2O_3? How many iron atoms are in one mole of Fe_2O_3?

4.6 Write all the mole-to-mole conversion factors that can be written based on the following chemical formulas: **(a)** SO_2, **(b)** As_2O_3, **(c)** K_2SO_4, **(d)** Na_2HPO_4.

4.7 Write all the mole-to-mole conversion factors that can be written based on the following chemical formulas: **(a)** Mn_3O_4, **(b)** Sb_2S_5, **(c)** $(NH_4)_2SO_4$, **(d)** Hg_2Cl_2,

4.8 What information is required to convert grams of a substance into moles of that same substance?

4.9 Why is the expression "1.0 mol of oxygen" ambiguous? Why doesn't a similar ambiguity exist in the expression "64 g of oxygen?"

4.10 The atomic mass of aluminum is 26.98. What specific conversion factors does this value make available for relating a mass of aluminum (in grams) and a quantity of aluminum given in moles?

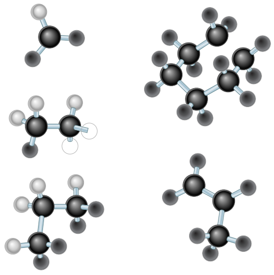
Empirical Formulas

4.11 In general, what fundamental information, obtained from experimental measurements, is required to calculate the empirical formula of a compound?

4.12 Why are empirical formulas always used for ionic compounds?

4.13 Under what circumstances can we change, or assign, subscripts in a chemical formula?

4.14 How many distinct empirical formulas are shown by the following models for compounds formed between elements *A* and *B*? Explain. (Element *A* is represented by a black sphere and element *B* by a light gray sphere.)



Avogadro's Number

4.15 How would Avogadro's number change if the atomic mass unit were to be redefined as 2×10^{-27} kg, exactly?

4.16 What information is required to convert grams of a substance into molecules of that same substance?

Stoichiometry with Balanced Equations

4.17 The balanced chemical equation for the combustion of propane, a common heating fuel, is

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Draw a molecular-level diagram of this chemical reaction. Use the color chart on page 11 to distinguish the atoms from each other.

4.18 Draw a molecular-level diagram for the reaction in which sulfur dioxide reacts with molecular oxygen to form sulfur trioxide. Be sure to write and balance the equation first. Use the color chart on page 11 to distinguish the atoms from each other.

4.19 When given the *unbalanced* equation

$$Na(s) + Cl_2(g) \longrightarrow NaCl(s)$$

and asked to balance it, student A wrote

$$Na(s) + Cl_2(g) \longrightarrow NaCl_2(s)$$

and student B wrote

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Both equations are balanced, but which student is correct? Explain why the other student's answer is incorrect.

4.20 Give a step-by-step procedure for estimating the number grams of A required to completely react with 10 moles of B, given the following information:

A and B react to form A_5B_2.

A has a molecular mass of 100.0.

B has a molecular mass of 200.0.

There are 6.02×10^{23} molecules of A in a mole of A.

Which of these pieces of information weren't needed?

4.21 If two substances react completely in a 1-to-1 ratio *both* by mass and by moles, what must be true about these substances?

4.22 What information is required to determine how many grams of sulfur would react with a gram of arsenic?

4.23 A mixture of 0.020 mol of Mg and 0.020 mol of Cl_2 reacted completely to form $MgCl_2$ according to the equation

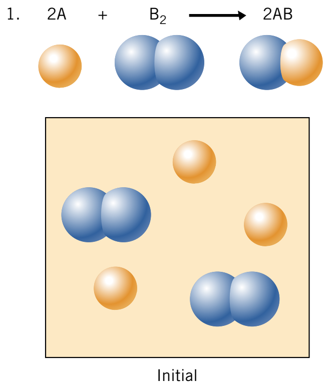
$$Mg + Cl_2 \longrightarrow MgCl_2$$

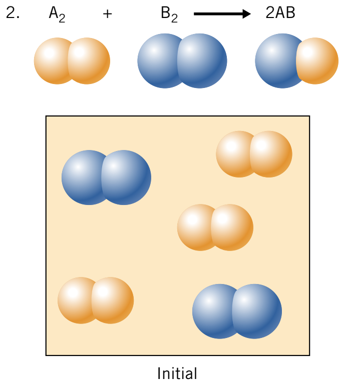
What information describes the *stoichiometry* of this reaction? What information gives the *scale* of the reaction?

4.24 In a report to a supervisor, a chemist described an experiment in the following way: "0.0800 mol of H_2O_2 decomposed into 0.0800 mol of H_2O and 0.0400 mol of O_2." Express the chemistry and stoichiometry of this reaction by a conventional chemical equation.

4.25 On April 16, 1947, in Texas City, Texas, two cargo ships, the *Grandcamp* and the *High Flier*, were each loaded with approximately 2000 tons of ammonium nitrate fertilizer. The *Grandcamp* caught fire and exploded, followed by the *High Flier*. More than 600 people were killed and one-third of the city was destroyed. Considering a much smaller mass, how would you count the number of N_2 molecules that could be produced after the explosion of 1.00 kg of NH_4NO_3?

4.26 Molecules containing *A* and *B* react to form *AB* as shown below. Based on the equations and the contents of the boxes labeled "Initial," sketch for each reaction the molecular models of what is present after the reaction is over. (In both cases, the species *B* exists as B_2. In reaction 1, *A* is monatomic; in reaction 2, *A* exists as diatomic molecules A_2.)





Review Problems

The Mole Concept and Stoichiometric Equivalencies

4.27 In what smallest whole-number ratio must N and O atoms combine to make dinitrogen tetroxide, N_2O_4? What is the mole ratio of the elements in this compound?

4.28 In what atom ratio are the elements present in methane, CH_4 (the chief component of natural gas)? In what mole ratio are the atoms of the elements present in this compound?

4.29 How many moles of tantalum atoms correspond to 1.56×10^{21} atoms of tantalum?

4.30 How many moles of iodine molecules correspond to 1.80×10^{24} molecules of I_2?

4.31 Sucrose (table sugar) has the formula $C_{12}H_{22}O_{11}$. In this compound, what is the

- **(a)** atom ratio of C to H?
- **(b)** mole ratio of C to O?
- **(c)** atom ratio of H to O?
- **(d)** mole ratio of H to O?

4.32 Nail polish remover is usually the volatile liquid ethyl acetate, $CH_3COOC_2H_5$. In this compound, what is the

- **(a)** atom ratio of C to O?
- **(b)** mole ratio of C to O?
- **(c)** atom ratio of C to H?
- **(d)** mole ratio of C to H?

4.33 How many moles of Bi atoms are needed to combine with 1.58 mol of O atoms to make bismuth oxide, Bi_2O_3?

4.34 How many moles of vanadium atoms, V, are needed to combine with 0.565 mol of O atoms to make vanadium pentoxide, V_2O_5?

4.35 How many moles of Cr are in 2.16 mol of Cr_2O_3?

4.36 How many moles of O atoms are in 4.25 mol of calcium carbonate, $CaCO_3$, the chief constituent of seashells?

4.37 Aluminum sulfate, $Al_2(SO_4)_3$, is a compound used in sewage treatment plants.

- **(a)** Construct a pair of conversion factors that relate moles of aluminum to moles of sulfur for this compound.
- **(b)** Construct a pair of conversion factors that relate moles of sulfur to moles of $Al_2(SO_4)_3$.
- **(c)** How many moles of Al are in a sample of this compound if the sample also contains 0.900 mol S?
- **(d)** How many moles of S are in 1.16 mol $Al_2(SO_4)_3$?

4.38 Magnetite is a magnetic iron ore. Its formula is Fe_3O_4.

- **(a)** Construct a pair of conversion factors that relate moles of Fe to moles of Fe_3O_4.
- **(b)** Construct a pair of conversion factors that relate moles of Fe to moles of O in Fe_3O_4.
- **(c)** How many moles of Fe are in 2.75 mol of Fe_3O_4?
- **(d)** If this compound could be prepared from Fe_2O_3 and O_2, how many moles of Fe_2O_3 would be needed to prepare 4.50 mol Fe_3O_4?

4.39 How many moles of H_2 and N_2 can be formed by the decomposition of 0.145 mol of ammonia, NH_3?

4.40 How many moles of S are needed to combine with 0.225 mol Al to give Al_2S_3?

ILW **4.41** How many moles of UF_6 would have to be decomposed to provide enough fluorine to prepare 1.25 mol of CF_4? (Assume sufficient carbon is available.)

4.42 How many moles of Fe_3O_4 are required to supply enough iron to prepare 0.260 mol Fe_2O_3? (Assume sufficient oxygen is available.)

4.43 How many atoms of carbon are combined with 4.13 moles of hydrogen atoms in a sample of the compound propane, C_3H_8? (Propane is used as the fuel in gas barbecues.)

4.44 How many atoms of hydrogen are found in 2.31 mol of propane, C_3H_8?

4.45 What is the total number of C, H, and O atoms in 0.260 moles of glucose, $C_6H_{12}O_6$?

4.46 What is the total number of N, H, and O atoms in 0.356 mol of ammonium nitrate, NH_4NO_3, an important fertilizer?

Measuring Moles of Elements and Compounds

4.47 How many atoms are in 6.00 g of carbon-12?

OH **4.48** How many atoms are in 1.50 mol of carbon-12? How many grams does this much carbon-12 weigh?

4.49 Determine the mass in grams of each of the following: **(a)** 1.35 mol Fe, **(b)** 24.5 mol O, **(c)** 0.876 mol Ca.

4.50 Determine the mass in grams of each of the following: **(a)** 0.546 mol S, **(b)** 3.29 mol N, **(c)** 8.11 mol Al.

4.51 A nanotechnology experiment requires 2×10^{12} atoms of potassium. What is the mass of this sample?

4.52 What is the mass, in grams, of 4×10^{17} atoms of gold present in one nanoparticle?

4.53 How many moles of nickel are in 17.7 g of Ni?

4.54 How many moles of chromium are in 85.7 g of Cr?

4.55 Calculate the formula mass of each of the following to the maximum number of significant figures possible using the table of atomic masses inside the front cover.

- **(a)** $NaHCO_3$
- **(b)** $(NH_4)_2CO_3$
- **(c)** $CuSO_4 \cdot 5H_2O$
- **(d)** potassium dichromate
- **(e)** aluminum sulfate

4.56 Calculate the formula mass of each of the following to the maximum number of significant figures possible using the table of atomic masses inside the front cover.

- **(a)** calcium nitrate
- **(b)** $Pb(C_2H_5)_4$
- **(c)** $Na_2SO_4 \cdot 10H_2O$
- **(d)** $Fe_4[Fe(CN)_6]_3$
- **(e)** magnesium phosphate

4.57 Calculate the mass in grams of the following.

- **(a)** 1.25 mol $Ca_3(PO_4)_2$
- **(b)** 0.625 mmol iron(III) nitrate

(c) 0.600 μmol C_4H_{10}

(d) 1.45 mol ammonium carbonate

4.58 What is the mass in grams of the following?

(a) 0.754 mol zinc chloride

(b) 0.194 μmol potassium chlorate

(c) 0.322 mmol $POCl_3$

(d) 4.31×10^{-3} mol $(NH_4)_2HPO_4$

4.59 Calculate the number of moles of each compound in the following samples.

(a) 21.5 g calcium carbonate

(b) 1.56 ng NH_3

(c) 16.8 g strontium nitrate

(d) 6.98 μg Na_2CrO_4

4.60 Calculate the number of moles of each compound in the following samples.

(a) 9.36 g calcium hydroxide

(b) 38.2 kg lead(II)sulfate

(c) 4.29 g H_2O_2

(d) 4.65 mg $NaAuCl_4$

ILW **4.61** One sample of CaC_2 contains 0.150 mol of carbon. How many moles and how many grams of calcium are also in the sample? [Calcium carbide, CaC_2, was once used to make signal flares for ships. Water dripped onto CaC_2 reacts to give acetylene (C_2H_2), which burns brightly.]

OH **4.62** How many moles of iodine are in 0.500 mol of $Ca(IO_3)_2$? How many grams of calcium iodate are needed to supply this much iodine? [Iodized salt contains a trace amount of calcium iodate, $Ca(IO_3)_2$, to help prevent a thyroid condition called goiter.]

4.63 How many moles of nitrogen, N, are in 0.650 mol of ammonium carbonate? How many grams of this compound supply this much nitrogen?

4.64 How many moles of nitrogen, N, are in 0.556 mol of ammonium nitrate? How many grams of this compound supply this much nitrogen?

4.65 How many kilograms of a fertilizer made of pure $(NH_4)_2CO_3$ would be required to supply 1 kilogram of nitrogen to the soil?

4.66 How many kilograms of a fertilizer made of pure P_2O_5 would be required to supply 1 kilogram of phosphorus to the soil?

Percentage Composition

4.67 Calculate the percentage composition by mass for each of the following:

(a) sodium dihydrogen phosphate

(b) $NH_4H_2PO_4$

(c) $(CH_3)_2CO$

(d) calcium sulfate dihydrate

(e) $CaSO_4 \cdot 2H_2O$

4.68 Calculate the percentage composition by mass of each of the following: **(a)** $(CH_3)_2N_2H_2$ **(b)** $CaCO_3$ **(c)** iron(III) nitrate **(d)** C_3H_8 **(e)** aluminum sulfate

4.69 Which has a higher percentage of oxygen: morphine ($C_{17}H_{19}NO_3$) or heroin ($C_{21}H_{23}NO_5$)?

4.70 Which has a higher percentage of nitrogen: carbamazepine ($C_{15}H_{12}N_2O$) or carbetapentane ($C_{20}H_{31}NO_3$)?

4.71 Freon is a trade name for a group of gaseous compounds once used as propellants in aerosol cans. Which has a higher percentage of chlorine: Freon-12 (CCl_2F_2) or Freon 141b ($C_2H_3Cl_2F$)?

4.72 Which has a higher percentage of fluorine: Freon-12 (CCl_2F_2) or Freon 113 ($C_2Cl_3F_3$)?

OH **4.73** It was found that 2.35 g of a compound of phosphorus and chlorine contained 0.539 g of phosphorus. What are the percentages by mass of phosphorus and chlorine in this compound?

4.74 An analysis revealed that 5.67 g of a compound of nitrogen and oxygen contained 1.47 g of nitrogen. What are the percentages by mass of nitrogen and oxygen in this compound?

4.75 Phencyclidine ("angel dust") is $C_{17}H_{25}N$. A sample suspected of being this illicit drug was found to have a percentage composition of 84.71% C, 10.42% H, and 5.61% N. Do these data acceptably match the theoretical data for phencyclidine?

4.76 The hallucinogenic drug LSD has the molecular formula $C_{20}H_{25}N_3O$. One suspected sample contained 74.07% C, 7.95% H, and 9.99% N.

(a) What is the percentage of O in the sample?

(b) Are these data consistent for LSD?

4.77 How many grams of O are combined with 7.14×10^{21} atoms of N in the compound dinitrogen pentoxide?

4.78 How many grams of C are combined with 4.25×10^{23} atoms of H in the compound C_5H_{12}?

Empirical Formulas

4.79 Write empirical formulas for the following compounds.

(a) S_2Cl_2 **(c)** NH_3 **(e)** H_2O_2

(b) $C_6H_{12}O_6$ **(d)** As_2O_6

4.80 What are the empirical formulas of the following compounds?

(a) $C_2H_4(OH)_2$ **(c)** C_4H_{10} **(e)** C_2H_5OH

(b) $H_2S_2O_8$ **(d)** B_2H_6

4.81 Quantitative analysis of a sample of sodium pertechnetate with a mass of 0.896 g found 0.111 g of sodium and 0.477 g of technetium. The remainder was oxygen. Calculate the empirical formula of sodium pertechnetate. (Radioactive sodium pertechnetate is used as a brain-scanning agent in medicine.)

4.82 A sample of Freon was found to contain 0.423 g of C, 2.50 g of Cl, and 1.34 g of F. What is the empirical formula of this compound?

4.83 A dry-cleaning fluid composed of only carbon and chlorine was found to be composed of 14.5% C and 85.5% Cl (by mass). What is the empirical formula of this compound?

4.84 One compound of mercury with a molar mass of 519 contains 77.26% Hg, 9.25% C, and 1.17% H (with the balance being O). Calculate the empirical and molecular formulas.

4.85 Cinnamic acid, a compound related to the flavor component of cinnamon, is 72.96% carbon, 5.40% hydrogen, and the rest is oxygen. What is the empirical formula of this acid?

4.86 Vanillin, a compound used as a flavoring agent in food products, has the following percentage composition: 64.2% C, 5.26% H, and 31.6% O. What is the empirical formula of vanillin?

ILW **4.87** When 0.684 g of an organic compound containing only carbon, hydrogen, and oxygen was burned in oxygen, 1.312 g of CO_2 and 0.805 g of H_2O were obtained. What is the empirical formula of the compound?

4.88 Methyl ethyl ketone (often abbreviated MEK) is a powerful solvent with many commercial uses. A sample of this compound (which contains only C, H, and O) weighing 0.822 g was burned in oxygen to give 2.01 g of CO_2 and 0.827 g of H_2O. What is the empirical formula for MEK?

4.89 When 6.853 mg of a sex hormone was burned in a combustion analysis, 19.73 mg of CO_2 and 6.391 mg of H_2O were obtained. What is the empirical formula of the compound?

4.90 When a sample of a compound in the vitamin D family was burned in a combustion analysis, 5.983 mg of the compound gave 18.490 mg of CO_2 and 6.232 mg of H_2O. What is the empirical formula of the compound?

Molecular Formulas

4.91 The following are empirical formulas and the masses per mole for three compounds. What are their molecular formulas?

(a) NaS_2O_3; 270.4 g/mol
(b) C_3H_2Cl; 147.0 g/mol
(c) C_2HCl; 181.4 g/mol

4.92 The following are empirical formulas and the masses per mole for three compounds. What are their molecular formulas?

(a) Na_2SiO_3; 732.6 g/mol
(b) $NaPO_3$; 305.9 g/mol
(c) CH_3O; 62.1 g/mol

4.93 The compound described in Problem 4.89 was found to have a molecular mass of 290. What is its molecular formula?

4.94 The compound described in Problem 4.90 was found to have a molecular mass of 399. What is the molecular formula of this compound?

ILW **4.95** A sample of a compound of mercury and bromine with a mass of 0.389 g was found to contain 0.111 g bromine. Its molecular mass was found to be 561. What are its empirical and molecular formulas?

4.96 A 0.6662 g sample of "antimonal saffron," which is a red pigment used in painting, was found to contain 0.4017 g of antimony. The remainder was sulfur. The formula mass of this compound is 404. What are the empirical and molecular formulas of this pigment?

4.97 A sample of a compound of C, H, N, and O, with a mass of 0.6216 g was found to contain 0.1735 g of C, 0.01455 g of H, and 0.2024 g of N. Its formula mass is 129. Calculate its empirical and molecular formulas.

4.98 Strychnine, a deadly poison, has a formula mass of 334 and a percentage composition of 75.42% C, 6.63% H, 8.38% N, and the balance oxygen. Calculate the empirical and molecular formulas of strychnine.

Balancing Chemical Equations

4.99 A balanced chemical equation contains the term "$2Ba(OH)_2 \cdot 8H_2O$." How many atoms of each element does this represent in the molecular view? How many moles of each element does this represent on the laboratory scale?

4.100 A balanced chemical equation contains the term "$3Ca_3(PO_4)_2$." How many atoms of each element does this represent in the molecular view? How many moles of each element does this represent on the laboratory scale?

OH **4.101** Write the equation that expresses in acceptable chemical shorthand the following statement: "Iron can be made to react with molecular oxygen to give iron(III) oxide."

4.102 The conversion of one air pollutant, nitrogen monoxide, produced in vehicle engines, into another pollutant, nitrogen dioxide, occurs when nitrogen monoxide reacts with molecular oxygen in the air. Write the balanced equation for this reaction.

4.103 Balance the following equations.

(a) Calcium hydroxide reacts with hydrogen chloride to form calcium chloride and water.

(b) Silver nitrate and calcium chloride react to form calcium nitrate and silver chloride.

(c) Lead nitrate reacts with sodium sulfate to form lead sulfate and sodium nitrate.

(d) Iron(III) oxide and carbon react to form iron and carbon dioxide.

(e) Butane reacts with oxygen to form carbon dioxide and water.

4.104 Balance the following equations.

(a) $SO_2 + O_2 \longrightarrow SO_3$
(b) $NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$
(c) $P_4O_{10} + H_2O \longrightarrow H_3PO_4$
(d) $Fe_2O_3 + H_2 \longrightarrow Fe + H_2O$
(e) $Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$

4.105 Balance the following equations.

(a) $Mg(OH)_2 + HBr \longrightarrow MgBr_2 + H_2O$

(b) $HCl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O$

(c) $Al_2O_3 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2O$

(d) $KHCO_3 + H_3PO_4 \longrightarrow K_2HPO_4 + H_2O + CO_2$

(e) $C_9H_{20} + O_2 \longrightarrow CO_2 + H_2O$

4.106 Balance the following equations.

(a) $CaO + HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$

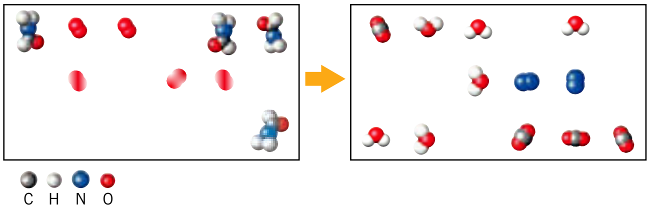
(b) $Na_2CO_3 + Mg(NO_3)_2 \longrightarrow MgCO_3 + NaNO_3$

(c) $(NH_4)_3PO_4 + NaOH \longrightarrow Na_3PO_4 + NH_3 + H_2O$

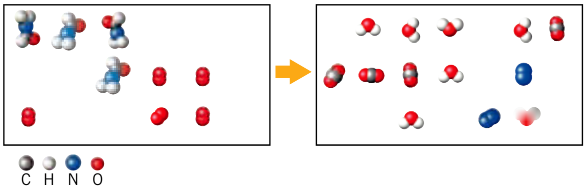
(d) $LiHCO_3 + H_2SO_4 \longrightarrow Li_2SO_4 + H_2O + CO_2$

(e) $C_4H_{10}O + O_2 \longrightarrow CO_2 + H_2O$

4.107 Using the diagram below, write the balanced chemical equation.



4.108 Using the diagram below, write the balanced chemical equation.



Stoichiometry Based on Chemical Equations

4.109 Chlorine is used by textile manufacturers to bleach cloth. Excess chlorine is destroyed by its reaction with sodium thiosulfate, $Na_2S_2O_3$, as follows.

$$Na_2S_2O_3(aq) + 4Cl_2(g) + 5H_2O \longrightarrow 2NaHSO_4(aq) + 8HCl(aq)$$

(a) How many moles of $Na_2S_2O_3$ are needed to react with 0.12 mol of Cl_2?

(b) How many moles of HCl can form from 0.12 mol of Cl_2?

(c) How many moles of H_2O are required for the reaction of 0.12 mol of Cl_2?

(d) How many moles of H_2O react if 0.24 mol HCl is formed?

4.110 The octane in gasoline burns according to the following equation.

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

(a) How many moles of O_2 are needed to react fully with 6.84 mol of octane?

(b) How many moles of CO_2 can form from 0.511 mol of octane?

(c) How many moles of water are produced by the combustion of 8.20 mol of octane?

(d) If this reaction is used to synthesize 6.00 mol of CO_2, how many moles of oxygen are needed? How many moles of octane?

4.111 The following reaction is used to extract gold from pretreated gold ore:

$$2Au(CN)_2^-(aq) + Zn(s) \longrightarrow 2Au(s) + Zn(CN)_4^{2-}(aq)$$

(a) How many grams of Zn are needed to react with 0.11 mol of $Au(CN)_2^-$?

(b) How many grams of Au can form from 0.11 mol of $Au(CN)_2^-$?

(c) How many grams of $Au(CN)_2^-$ are required for the reaction of 0.11 mol of Zn?

OH **4.112** Propane burns according to the following equation.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

(a) How many grams of O_2 are needed to react fully with 3.45 mol of propane?

(b) How many grams of CO_2 can form from 0.177 mol of propane?

(c) How many grams of water are produced by the combustion of 4.86 mol of propane?

4.113 The incandescent white of a fireworks display is caused by the reaction of phosphorus with O_2 to give P_4O_{10}.

(a) Write the balanced chemical equation for the reaction.

(b) How many grams of O_2 are needed to combine with 6.85 g of P?

(c) How many grams of P_4O_{10} can be made from 8.00 g of O_2?

(d) How many grams of P are needed to make 7.46 g of P_4O_{10}?

4.114 The combustion of butane, C_4H_{10}, produces carbon dioxide and water. When one sample of C_4H_{10} was burned, 4.46 g of water was formed.

(a) Write the balanced chemical equation for the reaction.

(b) How many grams of butane were burned?

(c) How many grams of O_2 were consumed?

(d) How many grams of CO_2 were formed?

ILW **4.115** In *dilute* nitric acid, HNO_3, copper metal dissolves according to the following equation.

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O$$

How many grams of HNO_3 are needed to dissolve 11.45 g of Cu according to this equation?

4.116 The reaction of hydrazine, N_2H_4, with hydrogen peroxide, H_2O_2, has been used in rocket engines. One way these compounds react is described by the equation

$$N_2H_4 + 7H_2O_2 \longrightarrow 2HNO_3 + 8H_2O$$

According to this equation, how many grams of H_2O_2 are needed to react completely with 852 g of N_2H_4?

4.117 Oxygen gas can be produced in the laboratory by decomposition of hydrogen peroxide (H_2O_2):

$$2H_2O_2 \longrightarrow 2H_2O + O_2(g)$$

How many kg of O_2 can be produced from 1.0 kg of H_2O_2?

4.118 Oxygen gas can be produced in the laboratory by decomposition of potassium chlorate ($KClO_3$):

$$KClO_3 \longrightarrow 2KCl + 3O_2(g)$$

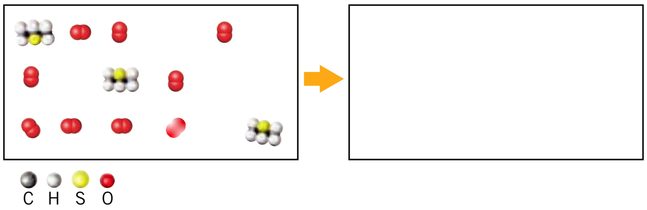
How many kg of O_2 can be produced from 1.0 kg of $KClO_3$?

Limiting Reactant Calculations

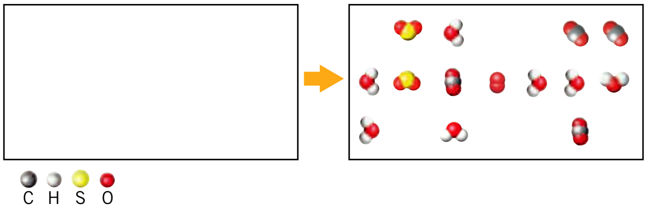
4.119 Using the balanced equation

$$2C_2H_6S(g) + 9O_2(g) \longrightarrow 4CO_2(g) + 2SO_2(g) + 6H_2O(g)$$

determine the number of SO_2 units formed in the following molecular representation.



4.120 Using the balanced chemical equation in Problem 4.119 and the diagram below, determine what the limiting reactant was.



4.121 The reaction of powdered aluminum and iron(III) oxide,

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

produces so much heat the iron that forms is molten. Because of this, railroads have used this reaction to provide molten iron to weld steel rails together when laying track. Suppose that in one batch of reactants 4.20 mol of Al was mixed with 1.75 mol of Fe_2O_3.

(a) Which reactant, if either, was the limiting reactant?

(b) Calculate the number of grams of iron that can be formed from this mixture of reactants.

4.122 Ethanol (C_2H_5OH) is synthesized for industrial use by the following reaction, carried out at very high pressure:

$$C_2H_4(g) + H_2O(g) \longrightarrow C_2H_5OH(l)$$

What is the maximum amount, in kg, of ethanol that can be produced when 1.62 kg of ethylene (C_2H_4) and 0.0148 kg of steam are placed into the reaction vessel?

ILW **4.123** Silver nitrate, $AgNO_3$, reacts with iron(III) chloride, $FeCl_3$,to give silver chloride, AgCl, and iron(III) nitrate, $Fe(NO_3)_3$. A solution containing 18.0 g of $AgNO_3$ was mixed with a solution containing 32.4 g of $FeCl_3$. How many grams of which reactant remains after the reaction is over?

4.124 Chlorine dioxide, ClO_2, has been used as a disinfectant in air-conditioning systems. It reacts with water according to the equation

$$6ClO_2 + 3H_2O \longrightarrow 5HClO_3 + HCl$$

If 142.0 g of ClO_2 is mixed with 38.0 g of H_2O, how many grams of which reactant remain if the reaction is complete?

ILW **4.125** Some of the acid in acid rain is produced by the following reaction:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

If a falling raindrop weighing 0.050 g comes into contact with 1.0 mg of $NO_2(g)$, how many milligrams of HNO_3 can be produced?

4.126 Phosphorus pentachloride reacts with water to give phosphoric acid and hydrogen chloride according to the following equation.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

In one experiment, 0.360 mol of PCl_5 was slowly added to 2.88 mol of water.

(a) Which reactant, if either, was the limiting reactant?

(b) How many grams of HCl were formed in the reaction?

Theoretical Yield and Percentage Yield

4.127 Barium sulfate, $BaSO_4$, is made by the following reaction.

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2NaNO_3(aq)$$

An experiment was begun with 75.00 g of $Ba(NO_3)_2$ and an excess of Na_2SO_4. After collecting and drying the product, 64.45 g of $BaSO_4$ was obtained. Calculate the theoretical yield and percentage yield of $BaSO_4$.

4.128 The Solvay process for the manufacture of sodium carbonate begins by passing ammonia and carbon dioxide through a solution of sodium chloride to make sodium bicarbonate and ammonium chloride. The equation for the overall reaction is

$$H_2O + NaCl + NH_3 + CO_2 \longrightarrow NH_4Cl + NaHCO_3$$

In the next step, sodium bicarbonate is heated to give sodium carbonate and two gases, carbon dioxide and steam.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

What is the theoretical yield of sodium carbonate, expressed in grams, if 120 g of NaCl was used in the first reaction? If 85.4 g of Na_2CO_3 was obtained, what was the percentage yield?

4.129 Aluminum sulfate can be made by the following reaction.

$$2AlCl_3(aq) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6HCl(aq)$$

It is quite soluble in water, so to isolate it the solution has to be evaporated to dryness. This drives off the volatile HCl, but the residual solid has to be heated to a little over 200 °C to drive off all of the water. In one experiment, 25.0 g of $AlCl_3$ was mixed with 30.0 g of H_2SO_4. Eventually, 28.46 g of pure $Al_2(SO_4)_3$ was isolated. Calculate the percentage yield.

4.130 The combustion of methyl alcohol in an abundant excess of oxygen follows the equation

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

When 6.40 g of CH_3OH was mixed with 10.2 g of O_2 and ignited, 6.12 g of CO_2 was obtained. What was the percentage yield of CO_2?

***4.131** The potassium salt of benzoic acid, potassium benzoate ($KC_7H_5O_2$), can be made by the action of potassium permanganate on toluene (C_7H_8) as follows.

$$C_7H_8 + 2KMnO_4 \longrightarrow KC_7H_5O_2 + 2MnO_2 + KOH + H_2O$$

If the yield of potassium benzoate cannot realistically be expected to be more than 71%, what is the minimum number of grams of toluene needed to produce 11.5 g of potassium benzoate?

OH ***4.132** Manganese(III) fluoride, MnF_3, can be prepared by the following reaction.

$$2MnI_2(s) + 13F_2(g) \longrightarrow 2MnF_3(s) + 4IF_5(l)$$

If the percentage yield of MnF_3 is always approximately 56%, how many grams of MnF_3 can be expected if 10.0 grams of each reactant is used in an experiment?

Additional Exercises

4.133 Mercury is an environmental pollutant because it can be converted by certain bacteria into the very poisonous substance dimethyl mercury, $(CH_3)_2Hg$. This compound ends up in the food chain and accumulates in the tissues of aquatic organisms, particularly fish, which renders them unsafe to eat. It is estimated that in the United States 263 tons of mercury are released into the atmosphere each year. If only 1.0 percent of this mercury is eventually changed to $(CH_3)_2Hg$, how many pounds of this compound are formed annually?

***4.134** Lead compounds are often highly colored and are toxic to mold, mildew, and bacteria, properties that in the past were useful for paints used before 1960. Today we know lead is very hazardous and it is not used in paint, however, old paint is still a problem. If a certain lead-based paint contains 14.5% $PbCr_2O_7$ and 73% of the paint evaporates as it dries, what mass of lead will be in a paint chip that weighs 0.15 g?

4.135 A superconductor is a substance that is able to conduct electricity without resistance, a property that is very desirable in the construction of large electromagnets. Metals have this property if cooled to temperatures a few degrees above absolute zero, but this requires the use of expensive liquid helium (boiling point 4 K). Scientists have discovered materials that become superconductors at higher temperatures, but they are ceramics. Their brittle nature has so far prevented them from being made into long wires. A recently discovered compound of magnesium and boron, which consists of 52.9 % Mg and 47.1 % B, shows special promise as a high-temperature superconductor because it is inexpensive to make and can be fabricated into wire relatively easily. What is the formula of this compound?

***4.136** A 0.1246 g sample of a compound of chromium and chlorine was dissolved in water. All of the chloride ion was then captured by silver ion in the form of AgCl. A mass of 0.3383 g of AgCl was obtained. Calculate the empirical formula of the compound of Cr and Cl.

***4.137** A compound of Ca, C, N, and S was subjected to quantitative analysis and formula mass determination, and the following data were obtained. A 0.250 g sample was mixed with Na_2CO_3 to convert all of the Ca to 0.160 g of $CaCO_3$. A 0.115 g sample of the compound was carried through a series of reactions until all of its S was changed to 0.344 g of $BaSO_4$. A 0.712 g sample was processed to liberate all of its N as NH_3, and 0.155 g of NH_3 was obtained. The formula mass was found to be 156. Determine the empirical and molecular formulas of this compound.

4.138 Ammonium nitrate will detonate if ignited in the presence of certain impurities. The equation for this reaction at a high temperature is

$$2NH_4NO_3(s) \xrightarrow{>300\ ^\circ C} 2N_2(g) + O_2(g) + 4H_2O(g)$$

Notice that all of the products are gases, so they occupy a vastly greater volume than the solid reactant.

(a) How many moles of *all* gases are produced from 1 mol of NH_4NO_3?

(b) If 1.00 ton of NH_4NO_3 exploded according to this equation, how many moles of *all* gases would be produced? (1 ton = 2000 lb.)

4.139 A lawn fertilizer is rated as 6.00% nitrogen, meaning 6.00 g of N in 100 g of fertilizer. The nitrogen is present in the form of urea, $(NH_2)_2CO$. How many grams of urea are present in 100 g of the fertilizer to supply the rated amount of nitrogen?

***4.140** Nitrogen is the "active ingredient" in many quick-acting fertilizers. You are operating a farm of 1500 acres to produce soybeans. Which of the following fertilizers will you choose as the most economical for your farm? **(a)** NH_4NO_3 at $625 for 25 kg; **(b)** $(NH_4)_2HPO_4$ at $55 for 1 kg; **(c)** urea, CH_4ON_2, at $60 for 5 kg; or **(d)** ammonia, NH_3 at $128 for 50 kg.

4.141 Based solely on the amount of available carbon, how many grams of sodium oxalate, $Na_2C_2O_4$, could be obtained from 125 g of C_6H_6? (Assume that no loss of carbon occurs in any of the reactions needed to produce the $Na_2C_2O_4$.)

4.142 According to NASA, the space shuttle's external fuel tank for the main propulsion system carries 1,361,936 lb of liquid oxygen and 227,641 lb of liquid hydrogen. During takeoff, these chemicals are consumed as they react to form water. If the reaction is continued until all of one reactant is gone, how many pounds of which reactant are left over?

***4.143** For a research project, a student decided to test the effect of the lead(II) ion (Pb^{2+}) on the ability of salmon eggs to hatch. This ion was obtainable from the water-soluble salt, lead(II) nitrate, $Pb(NO_3)_2$, which the student decided to make by the following reaction. (The desired product was to be isolated by the slow evaporation of the water.)

$$PbO(s) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + H_2O$$

Losses of product for various reasons were expected, and a yield of 86.0% was expected. In order to have 5.00 g of product at this yield, how many grams of PbO should be taken? (Assume that sufficient nitric acid, HNO_3, would be used.)

4.144 Chlorine atoms cause chain reactions in the stratosphere that destroy ozone that protects the Earth's surface from ultraviolet radiation. The chlorine atoms come from chlorofluorocarbons, compounds that contain carbon, fluorine, and chlorine, which were used for many years as refrigerants. One of these compounds is Freon-12, CF_2Cl_2. If a sample contains 1.0×10^{-9} g of Cl, how many grams of F should be present if all of the F and Cl atoms in the sample came from CF_2Cl_2 molecules?

***4.145** Lime, CaO, can be produced in two steps as shown in the equations below. If the percentage yield of the first step is 83.5% and the percentage yield of the second step is 71.4%, what is the expected overall percentage yield for producing CaO from $CaCl_2$?

$$CaCl_2(aq) + CO_2(g) + H_2O \longrightarrow CaCO_3(s) + 2HCl(aq)$$

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + H_2O(g)$$

Exercises in Critical Thinking

4.146 A newspaper story describing the local celebration of Mole Day on October 23 (selected for Avogadro's number, 6.02×10^{23}) attempted to give the readers a sense of the size of the number by stating that a mole of M&Ms would be equal to 18 tractor trailers full. Assuming that an M&M occupies a volume of about 0.5 cm^3, calculate the dimensions of a cube required to hold one mole of M&Ms. Would 18 tractor trailers be sufficient?

4.147 Suppose you had one mole of pennies and you were going to spend 500 million dollars each and every second until you spent your entire fortune. How many years would it take you to spend all this cash? (Assume 1 year = 365 days.)

4.148 Using the above two questions as examples, devise a creative way to demonstrate the size of the mole, or Avogadro's number.

4.149 List the different ways in which a chemist could use the information used to determine empirical formulas.

Chapters 1–4

Bringing It Together

Many of the fundamental concepts and problem-solving skills developed in the preceding chapters will carry forward into the rest of this book. Therefore, we recommend that you pause here to see how well you have grasped the concepts, how familiar you are with important terms, and how able you are at working chemistry problems.

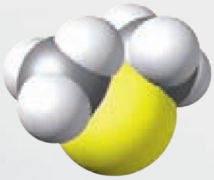
Don't be discouraged if some of the problems here seem to be difficult at first. Many require using tools developed in more than one chapter. In some cases, necessary data are not included in the problem, so you will need to refer to tables in the book, including those inside the front and back covers. For problems that require mathematical solutions, we recommend that you follow the approach used in the worked examples. Begin with an analysis of the problem. If you get stuck, keep in mind that all the neccessary tools have been discussed in the preceding chapters. Next, assemble the necessary tools and set up the required conversion factors needed to obtain the answers, and then proceed to the solution. Don't forget to check your answers!

1. A rectangular block of zinc was found to be 24.6 cm wide, 0.35140 m high, and 7,424 mm deep.
   - (a) How many significant figures are in each measurement?
   - (b) Calculate the volume of the block in units of cm^3. Be sure to express your answer to the correct number of significant figures.
   - (c) Calculate the volume of the zinc block in cubic feet.
   - (d) Zinc has a density of 7.140 g/cm^3. What is the mass of the block in kilograms?
   - (e) How many moles of zinc are contained in the block?
   - (f) If all of the zinc were converted to zinc phosphate, how many grams of this compound would be obtained?

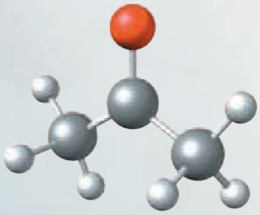
2. What is the difference between an atom and a molecule? What is the difference between a molecule and a mole? If you were forming a conversion factor, what relationship exists between molecules and moles?

3. If a 10.0 g sample of element *X* contains twice as many atoms as a 10.0 g sample of element *Y*, how does the atomic mass of *X* compare with the atomic mass of *Y*?

4. What is the percentage composition by mass of the substance shown below? How many molecules are in 12.0 g of this substance?



5. When the substance shown below burns in oxygen, the products are carbon dioxide and water. How many grams of water are obtained from burning 4.76 g of this substance?

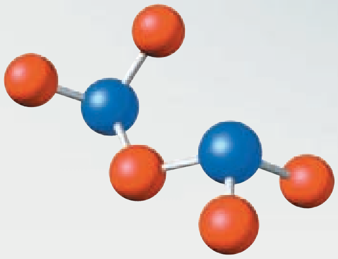


6. What is the total number of protons and electrons in one molecule of the substance described in Question 4?

7. Derive a single conversion factor that would enable you to convert a volume of 3.14 ft^3 into cubic centimeters (cm^3).

8. A silver nitrate solution was added to an aqueous solution of 1.223 g of an iron–chlorine compound. When dried and weighed, the silver chloride that formed weighed 3.243 g. What is the name of the iron–chlorine compound?

9. A sample of the compound shown below contains 5.22 g of nitrogen. How many grams of oxygen does it contain? What is the percentage by mass of nitrogen in the compound?



10. Ethanol, C_2H_5OH, is a renewable energy resource that is added to gasoline to help reduce the U.S. dependence on foreign oil imports. How many molecules of ethanol are in 1.00 fluid ounce of the liquid? The density of ethanol is 0.798 g/mL (1 fluid oz = 29.6 mL). How many grams of O_2 are needed for the complete combustion of 1.00 gallons of ethanol to give CO_2 and H_2O?

11. How did Dalton's atomic theory account for the law of conservation of mass? How did it explain the law of definite proportions?

12. What are the formula and name of the compound formed from chlorine and a substance in which the atoms contain 20 protons? What is the molar mass of this compound?

13. The atoms of one of the isotopes of plutonium, Pu, contain 94 protons, 110 neutrons, and 94 electrons. Write a symbol for this isotope that incorporates its mass number and atomic number. Write the symbol for a different isotope of plutonium.

14. Give chemical formulas for the following.
   - (a) potassium nitrate
   - (b) calcium carbonate
   - (c) cobalt(II) phosphate
   - (d) magnesium sulfite
   - (e) iron(III) bromide
   - (f) magnesium nitride
   - (g) aluminum selenide
   - (h) copper(II) perchlorate
   - (i) bromine pentafluoride
   - (j) dinitrogen pentaoxide
   - (k) strontium acetate
   - (l) ammonium dichromate
   - (m) copper(I) sulfide

15. Give chemical names for the following.
   - (a) $NaClO_3$
   - (b) $Ca_3(PO_4)_2$
   - (c) $NaMnO_4$
   - (d) AlP
   - (e) ICl_3
   - (f) PCl_3
   - (g) K_2CrO_4
   - (h) $Ca(CN)_2$
   - (i) $MnCl_2$
   - (j) $NaNO_2$
   - (k) $Fe(NO_3)_2$

16. For each of the following, indicate whether it is possible to see the item specified with the naked eye. If not, explain.

(a) A molar mass of iron
(b) An atom of iron
(c) A molecule of water
(d) A mole of water
(e) An ion of sodium
(f) A formula unit of sodium chloride

17. Which of the following are binary substances: Al_2O_3, Cl_2, MgO, NO_2, $NaClO_4$? Which are molecular and which are ionic?

18. If 2.56 g of chlorine, Cl_2, will be used to prepare dichlorine heptaoxide, how many moles and how many grams of molecular oxygen are needed?

19. How many grams of O_2 are consumed in the complete combustion of 25.0 mL of ethylene glycol, $C_2H_4(OH)_2$, which has a density of 1.11 g mL^{-1}? The products of the combustion are CO_2 and H_2O. How many molecules of CO_2 are formed in the reaction?

20. A sample of 0.5866 g of nicotine was analyzed and found to consist of 0.4343 g C, 0.05103 g H, and 0.1013 g N. Calculate the percentage composition of nicotine.

21. A compound of potassium had the following percentage composition: K, 37.56%; H, 1.940%; P, 29.79%. The rest was oxygen. Calculate the empirical formula of this compound (arranging the atomic symbols in the order K H P O.)

22. How many milliliters of pure nitric acid, HNO_3, are needed to react with 2.56 mol of Cu in the following reaction? The density of nitric acid is 1.51 g cm^{-3}.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

23. Under the right conditions, ammonia can be converted to nitrogen monoxide, NO, according to the following unbalanced equation.

$$NH_3 + O_2 \longrightarrow NO + H_2O$$

How many moles and how many grams of O_2 are needed to react with 56.8 g of ammonia by this reaction?

24. Dolomite is a mineral consisting of calcium carbonate and magnesium carbonate. When dolomite is strongly heated, its carbonates decompose to their oxides (CaO and MgO) and carbon dioxide is expelled.

(a) Write the separate equations for the decomposition of calcium carbonate and magnesium carbonate.

(b) When a dolomite sample with a mass of 5.78 g was heated strongly, the residue had a mass of 3.02 g. Calculate the masses in grams and the percentages of calcium carbonate and magnesium carbonate in this sample of dolomite.

25. Adipic acid, $C_6H_{10}O_4$, is a raw material for making nylon, and it can be prepared in the laboratory by the following reaction between cyclohexene, C_6H_{10}, and sodium dichromate, $Na_2Cr_2O_7$, in sulfuric acid, H_2SO_4.

$$3C_6H_{10}(l) + 4Na_2Cr_2O_7(aq) + 16H_2SO_4(aq) \longrightarrow 3C_6H_{10}O_4(s) + 4Cr_2(SO_4)_3(aq) + 4Na_2SO_4(aq) + 16H_2O$$

There are side reactions. These plus losses of product during its purification reduce the overall yield. A typical yield of purified adipic acid is 68.6%.

(a) To prepare 12.5 g of adipic acid in 68.6% yield requires how many grams of cyclohexene?

(b) The only available supply of sodium dichromate is its dihydrate, $Na_2Cr_2O_7 \cdot 2H_2O$. (Since the reaction occurs in an aqueous medium, the water in the dihydrate causes no problems, but it does contribute to the mass of what is taken of this reactant.) How many grams of this dihydrate are also required in the preparation of 12.5 g of adipic acid in a yield of 68.6%?

26. One of the ores of iron is hematite, Fe_2O_3, mixed with other rock. One sample of this ore is 31.4% hematite. How many tons of this ore are needed to make 1.00 ton of iron if the percentage recovery of iron from the ore is 91.5% (1 ton = 2000 lb)?

27. Gold occurs in the ocean in a range of concentration of 0.1 to 2 mg of gold per ton of seawater. Near one coastal city the gold concentration of the ocean is 1.5 mg/ton.

(a) How many tons of seawater have to be processed to obtain 1.0 troy ounce of gold if the recovery is 65% successful? (The troy ounce, 31.1 g, is the standard "ounce" in the gold trade.)

(b) If gold can be sold for $1152.84 per troy ounce, what is the breakeven point in the dollar cost per ton of processed seawater for extracting gold from the ocean at this location?

28. *C.I. Pigment Yellow 45* ("sideran yellow") is a pigment used in ceramics, glass, and enamel. When analyzed, a 2.164 g sample of this substance was found to contain 0.5259 g of Fe and 0.7345 g of Cr. The remainder was oxygen. Calculate the empirical formula of this pigment. What additional data are needed to calculate the molecular mass of this compound?

29. When 6.584 mg of one of the hydrates of sodium sulfate was heated so as to drive off all of its water of hydration, the residue of anhydrous sodium sulfate had a mass of 2.889 mg. What is the formula of the hydrate?

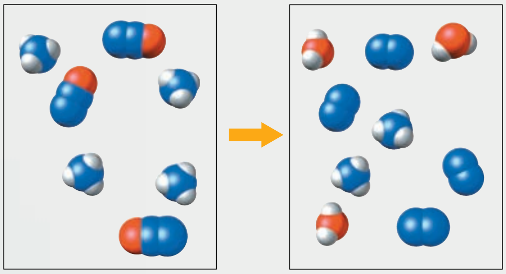
30. In an earlier problem we described the reaction of ammonia with oxygen to form nitrogen monoxide, NO:

$$NH_3 + O_2 \longrightarrow NO + H_2O \qquad \text{(unbalanced)}$$

How many moles and how many grams of NO could be formed from a mixture of 45.0 g of NH_3 and 58.0 g of O_2? How many grams of which reactant would remain unreacted?

31. A sample of 14.0 cm^3 of aluminum, in powdered form, was mixed with an excess of iron(III) oxide. A reaction between them was initiated that formed aluminum oxide and metallic iron. How many cubic centimeters of metallic iron were formed?

32. Give the balanced equation for the reaction shown below. Is there a limiting reactant? How many molecules of the excess reactant are left?



33. What principle forms the basis for the arrangement of elements in the periodic table? If the periodic table was arranged in a spiral, what elements would be to the right of helium, neon, argon, krypton, and radon, respectively?

5 Molecular View of Reactions in Aqueous Solutions

Chapter Outline

5.1 | Describing Solutions

5.2 | Electrolytes, Weak Electrolytes, and Nonelectrolytes

5.3 | Acids and Bases

5.4 | Acid–Base Nomenclature

5.5 | Double Replacement (Metathesis) Reactions

5.6 | Molarity

5.7 | Solution Stoichiometry

5.8 | Titrations and Chemical Analysis

The Coca-Cola shown in this photo is a complex mixture that contains, among other things, a small amount of phosphoric acid, which is added to provide just a bit of tartness to the beverage. Many of the foods we eat contain acids and many of the products we use around the house contain substances called bases. The nature of acids and bases and how they behave in aqueous solutions are among the topics discussed later in this chapter. (Photocuisine/Masterfile)

This Chapter in Context

Water is an amazing substance. Composed of just three atoms, it is one of the most common compounds on earth, and its ability to dissolve so many different kinds of materials is responsible, to a large degree, for the evolution of life as we know it. Our bodies are composed of approximately 60% water; it is the major component of the fluids in and around our cells, and it serves to transport nutrients throughout our systems.

A property of water that sets it apart from other liquids is its ability to dissolve many ionic compounds, enabling their particles to mix at the molecular level where they are able to easily react. In this chapter we will study in detail what happens when ionic substances dissolve in water, the nature of the chemical reactions they undergo, and the products that form. We will also introduce you to another important class of compounds called acids and bases, and we will examine the reactions of these substances in aqueous solutions. Finally, we will extend the principles of stoichiometry that you learned in Chapter 4 to deal quantitatively with chemical reactions in solution.

5.1 | Describing Solutions

Before we get to the meat of our subject, we first must define some terms. A **solution** is a homogeneous mixture in which the molecules or ions of the components freely intermingle (Figure 5.1). When a solution forms, at least two substances are involved. One is the *solvent* and all of the others are *solutes.* The **solvent** is the medium into which the solutes are mixed or dissolved. In this chapter we deal with *aqueous solutions*, so the solvent will be liquid water.[1] A **solute** is any substance dissolved in the solvent. It might be a gas, like the carbon dioxide dissolved in the Coca-Cola shown in the photo on the preceding page. Some solutes are liquids, like ethylene glycol dissolved in water to protect a car's radiator against freezing in the winter and boiling over in the summer. Solids, of course, can be solutes, like the sugar dissolved in lemonade or the salt dissolved in seawater.

■ When water is a component of a solution, it is usually considered to be the solvent even when it is present in small amounts.

To describe the composition of a solution, we often specify a **concentration**, which is the *ratio* of the amount of solute either to the amount of solvent or to the amount of solution. A **percentage concentration**, for example, is the number of grams of solute per 100 g of solution, a "solute-to-solution" ratio. Thus, the concentration of sodium chloride in seawater is often given as 3% NaCl, which means 3 g NaCl/100 g seawater.

The *relative* amounts of solute and solvent are often loosely given without specifying actual quantities. In a **dilute solution** the ratio of solute to solvent is small—such as when a few crystals of salt are dissolved in a glass of water. In a **concentrated solution**, the ratio of solute to solvent is large (Figure 5.2). Pancake syrup, for example, is a very concentrated solution of sugar in water.

Concentrated and dilute are relative terms. For example, a solution of 100 g of sugar in 100 mL of water is concentrated compared to one with just 10 g of sugar in 100 mL of water, but the latter solution is more concentrated than one that has 1 g of sugar in 100 mL of water.

Usually there is a limit to how much solute will dissolve in a solution. When a solution contains as much solute as it will hold at a given temperature, it is a **saturated solution** and any excess solute that's added simply sits at the bottom of the solution. The **solubility** of a solute is the amount required to give a saturated solution, usually expressed as grams dissolved in 100 g of solvent at a given temperature. The temperature must be specified because solubilities vary with temperature. A solution having less solute than required for saturation is called an **unsaturated solution.** It is able to dissolve more solute.

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[1] Liquid water is a typical and very common solvent, but the solvent can actually be in any physical state: solid, liquid, or gas.

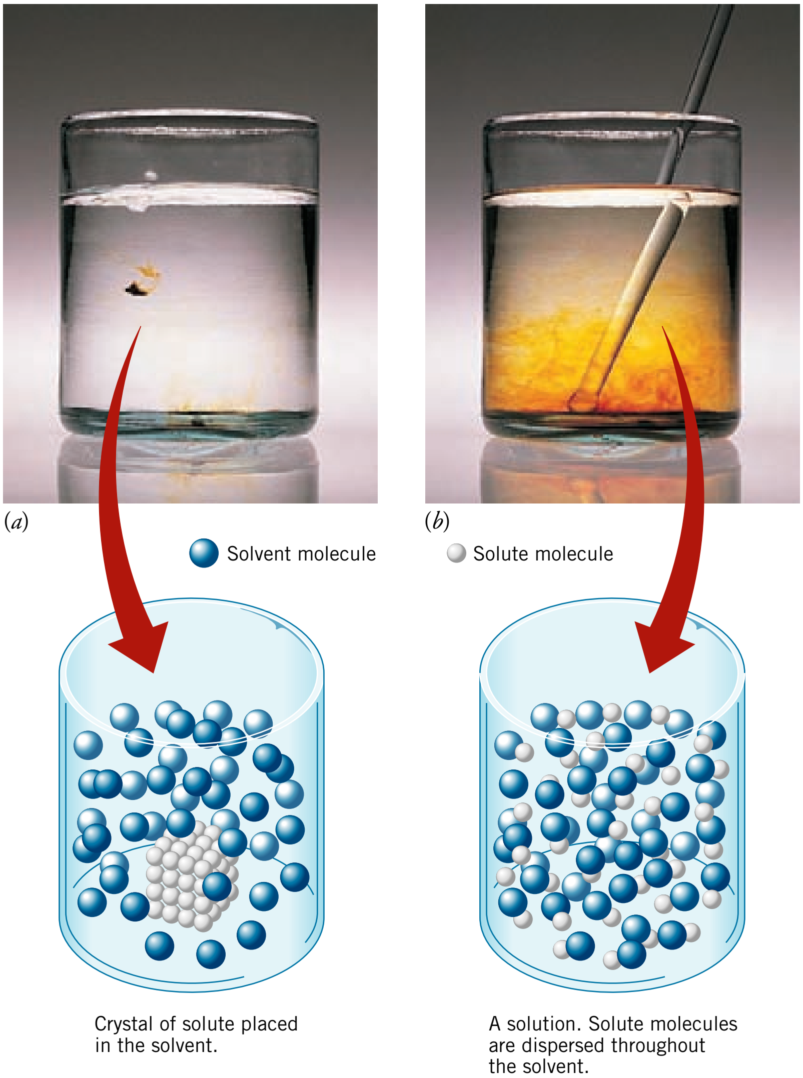

(*a*)
(*b*)
Solvent molecule
Solute molecule
Crystal of solute placed in the solvent.
A solution. Solute molecules are dispersed throughout the solvent.

Figure 5.1 | **Formation of a solution of iodine molecules in alcohol.** *(a)* A crystal of iodine, I_2, on its way to the bottom of the beaker is already beginning to dissolve, the purplish iodine crystal forming a reddish brown solution. In the hugely enlarged view beneath the photo, we see the iodine molecules still bound in a crystal. For simplicity, the solute and solvent particles are shown as spheres. *(b)* Stirring the mixture helps the iodine molecules to disperse in the solvent, as illustrated in the molecular view below the photo. The solution is commonly called "tincture of iodine." *(Richard Megna/Fundamental Photographs)*

In most cases, the solubility of a solute increases with temperature, so more solute can be dissolved by heating a saturated solution in the presence of excess solute. If the temperature of such a warm saturated solution is subsequently lowered, the additional solute should separate from the solution, and indeed, this tends to happen spontaneously. However, sometimes the solute doesn't separate, leaving us with a **supersaturated solution**, a solution that actually contains more solute than required for saturation. Supersaturated solutions are unstable and can only be prepared if there are no traces of undissolved solute. If even a tiny crystal of the solute is present or is added, the extra solute crystallizes (Figure 5.3). A solid that forms in a solution is called a **precipitate,** and a chemical reaction that produces a precipitate is called a **precipitation reaction.**

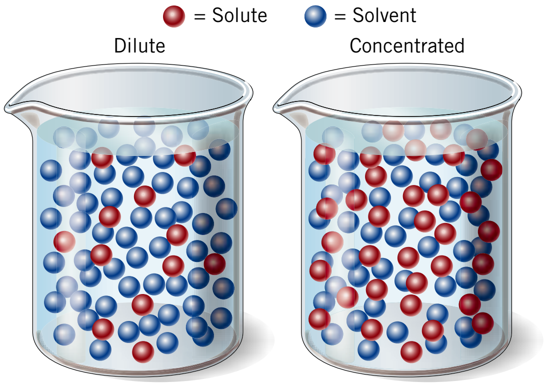


Figure 5.2 | **Dilute and concentrated solutions.** The dilute solution on the left has fewer solute molecules per unit volume than the more concentrated solution on the right.

5.2 | Electrolytes, Weak Electrolytes, and Nonelectrolytes

Water itself is a very poor electrical conductor because it consists of electrically neutral molecules that are unable to transport electrical charges. However, as we noted in Chapter 3, when an ionic compound dissolves in water the resulting solution conducts

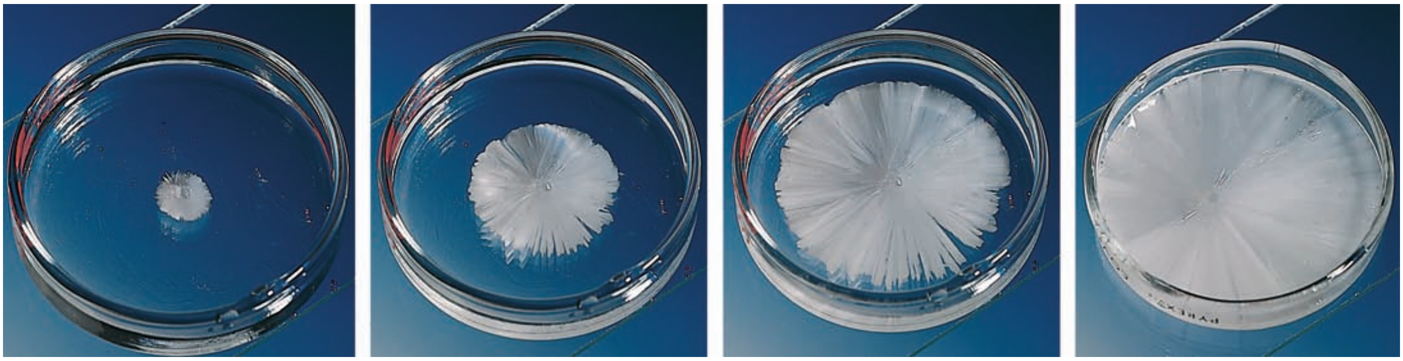
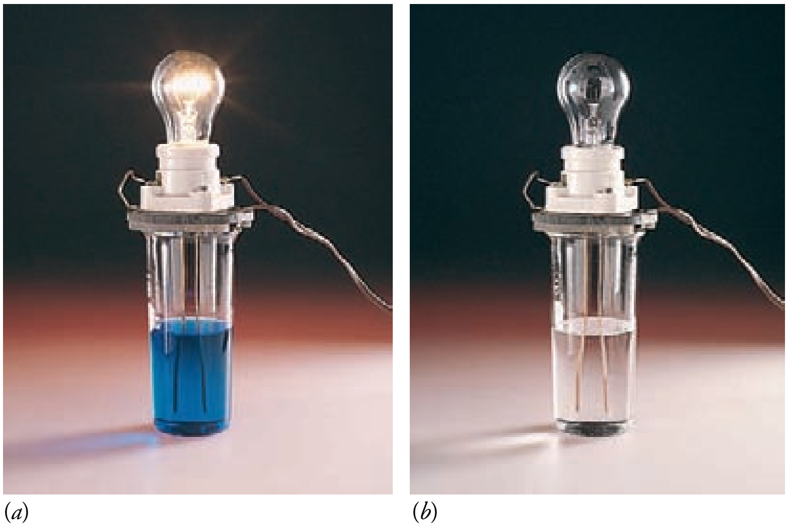


Figure 5.3 | **Crystallization.** When a small seed crystal of sodium acetate is added to a supersaturated solution of the compound, excess solute crystallizes rapidly until the solution is just saturated. The crystallization shown in this sequence took less than 10 seconds! *(Andy Washnik)*



(*a*) (*b*)

Figure 5.4 | **Electrical conductivity of solutions.** (*a*) The copper sulfate solution is a strong conductor of electricity, so $CuSO_4$ is classified as a strong electrolyte. (*b*) Neither sugar nor water is an electrolyte, so this sugar solution is a nonconductor. *(Michael Watson)*

- Solutions of electrolytes conduct electricity in a way that's different from metals. This is discussed more completely in Chapter 20.

- Ethylene glycol, $C_2H_4(OH)_2$, is a type of alcohol. Other alcohols, such as ethanol and methanol, are also nonelectrolytes.

electricity well. This is illustrated in Figure 5.4*a* for a solution of copper sulfate, $CuSO_4$.

Solutes such as $CuSO_4$, which yield electrically conducting aqueous solutions, are called **electrolytes**. Their ability to conduct electricity suggests the presence of electrically charged particles that are able to move within the solution. The generally accepted reason is that when an ionic compound dissolves in water, the ions separate from each other and enter the solution as more or less independent particles that are surrounded by molecules of the solvent. This change is called the **dissociation** (*breaking apart*) of the ionic compound, and is illustrated in Figure 5.5. In general, *we will assume that in water the dissociation of any* **salt** (*a term that applies to any ionic compound*) *is complete* and that the solution contains no undissociated formula units of the salt. Thus, an aqueous solution of $CuSO_4$ is really a solution that contains Cu^{2+} and SO_4^{2-} ions, with virtually no undissociated formula units of $CuSO_4$. Because solutions of ionic compounds contain so many freely moving ions, they are strong conductors of electricity. Therefore, salts are said to be **strong electrolytes.**

Many ionic compounds have low solubilities in water. An example is AgBr, the light-sensitive compound in most photographic film. Although only a tiny amount of this compound dissolves in water, all of it that does dissolve is completely dissociated. However, because of the extremely low solubility, the number of ions in the solution is extremely small and the solution doesn't conduct electricity well. Nevertheless, it is still convenient to think of AgBr as a strong electrolyte because it serves to remind us that salts are completely dissociated in aqueous solution.

Aqueous solutions of most molecular, covalently bonded compounds do not conduct electricity, and such solutes are called **nonelectrolytes**. Examples are sugar (Figure 5.4*b*) and ethylene glycol (the solute in antifreeze solutions). Both consist of uncharged molecules that stay intact and simply intermingle with water molecules when they dissolve (Figure 5.6).

Dissociation Reactions

A convenient way to describe the dissociation of an ionic compound is with a chemical equation. Thus, for the dissociation of calcium chloride in water we write

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

We use the symbol (*aq*) after a charged particle to mean that it is **hydrated** (*surrounded by water molecules in the solution*). By writing the formulas of the ions separately, we mean

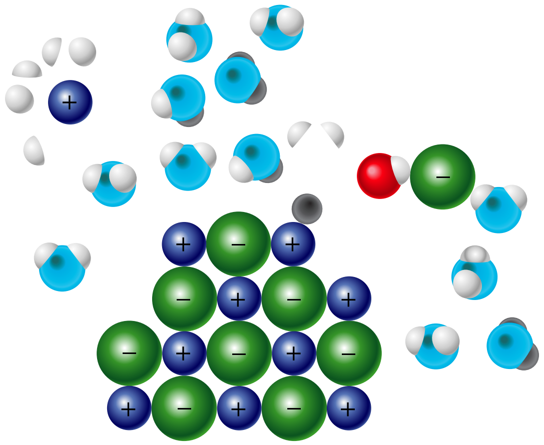


Figure 5.5 | **Dissociation of an ionic compound as it dissolves in water.** Ions separate from the solid and become surrounded by water molecules. The ions are said to be hydrated. In the solution the ions are able to move freely, which enables the solution to conduct electricity.

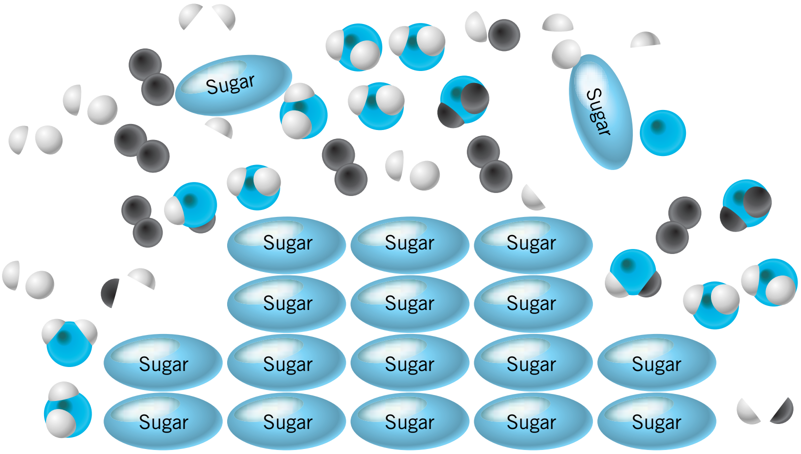


Figure 5.6 | **Formation of an aqueous solution of a nonelectrolyte.** When a nonelectrolyte dissolves in water, the molecules of solute separate from each other and mingle with the water molecules. The solute molecules stay intact and do not dissociate into smaller particles.

that they are essentially independent of each other in the solution. Notice that each formula unit of $CaCl_2(s)$ releases three ions, one $Ca^{2+}(aq)$ and two $Cl^-(aq)$.

Often, when the context is clear that the system is aqueous, the symbols (s) and (aq) are omitted. They are "understood." You should not be disturbed, therefore, when you see an equation such as

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

Polyatomic ions generally remain intact as dissociation occurs. When copper sulfate dissolves, for example, both Cu^{2+} and SO_4^{2-} ions are released.

$$CuSO_4(s) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

■ Be sure you know the formulas and charges on the polyatomic ions listed in Table 3.5 on page 84.

Example 5.1

Writing the Equation for the Dissociation of an Ionic Compound

Ammonium sulfate is used as a fertilizer to supply nitrogen to crops. Write the equation for the dissociation of this compound when it dissolves in water.

■ **Analysis:** This is actually a two-part problem. First, we have to write the correct formula for ammonium sulfate. Then we have to write the equation of the dissociation.

■ **Assembling the Tools:** First we need the formula for ammonium sulfate, which means we need to know the formulas and charges of the ions that make up the salt. You should already know this information, but if you forgot it, the tool to use is Table 3.5 in Section 3.4. To write the equation, we need to follow the style presented above.

Solution: In this case, the cation is NH_4^+ (ammonium ion) and the anion is SO_4^{2-} (sulfate ion). The correct formula of the compound is therefore $(NH_4)_2SO_4$, which means there are *two* NH_4^+ ions for each SO_4^{2-} ion. We have to be sure to indicate this in the ionic equation.

We write the formula for the solid on the left of the equation and indicate its state by (*s*). The ions are written on the right side of the equation and are shown to be in aqueous solution by the symbol (*aq*) following their formulas.

$$(NH_4)_2SO_4(s) \longrightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

The subscript 2 becomes the coefficient for NH_4^+.

Is the Answer Reasonable? There are two things to check when writing equations such as this. First, be sure you have the correct formulas for the ions, including their charges. Second, be sure you've indicated the number of ions of each kind that comes from one formula unit when the compound dissociates. Performing these checks here confirms we've solved the problem correctly.

Practice Exercises

5.1 | Write equations that show the dissociation of the following compounds in water: (a) $FeCl_3$ and (b) potassium phosphate. (*Hint:* Identify the ions present in each compound.)

5.2 | Write equations that show what happens when the following solid ionic compounds dissolve in water: (a) $MgCl_2$, (b) $Al(NO_3)_3$, and (c) sodium carbonate.

Equations for Ionic Reactions

Often, ionic compounds react with each other when their aqueous solutions are combined. For example, when solutions of lead(II) nitrate, $Pb(NO_3)_2$, and potassium iodide, KI, are mixed, a bright yellow precipitate of lead(II) iodide, PbI_2, forms (Figure 5.7). The chemical equation for the reaction is

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq) \tag{5.1}$$

where we have noted the insolubility of PbI_2 by writing (*s*) following its formula. This is called a **molecular equation** because all the formulas are written with the ions together, as if

CHEMISTRY OUTSIDE THE CLASSROOM 5.1

Painful Precipitates—Kidney Stones

Each year, more than a million people in the United States are hospitalized because of very painful kidney stone attacks. Kidney stone is a hard mass developed from crystals that separate from the urine and build up on the inner surfaces of the kidney. The formation of the stones is caused primarily by the buildup of Ca^{2+}, $C_2O_4^{2-}$, and PO_4^{3-} ions in the urine. When the concentrations of these ions become large enough, the urine becomes supersaturated with respect to calcium oxalate and/or calcium phosphate and precipitates begin to form (70% to 80% of all kidney stones are made up of calcium oxalate and phosphate). If the crystals remain tiny enough, they can travel through the urinary tract and pass out of the body in the urine without being noticed. Sometimes, however, they continue to grow without being passed and can cause intense pain if they become stuck in the urinary tract.

Kidney stones don't all look alike. Their color depends on what substances are mixed with the inorganic precipitates (e.g., proteins or blood). Most are yellow or brown, as seen in the accompanying photo, but they can be tan, gold, or even black. Stones can be round, jagged, or even have branches. They vary in size from mere specks to pebbles to stones as big as golf balls!

A calcium oxalate kidney stone. Kidney stones such as this can be extremely painful. *(Custom Medical Stock Photo, Inc.)*

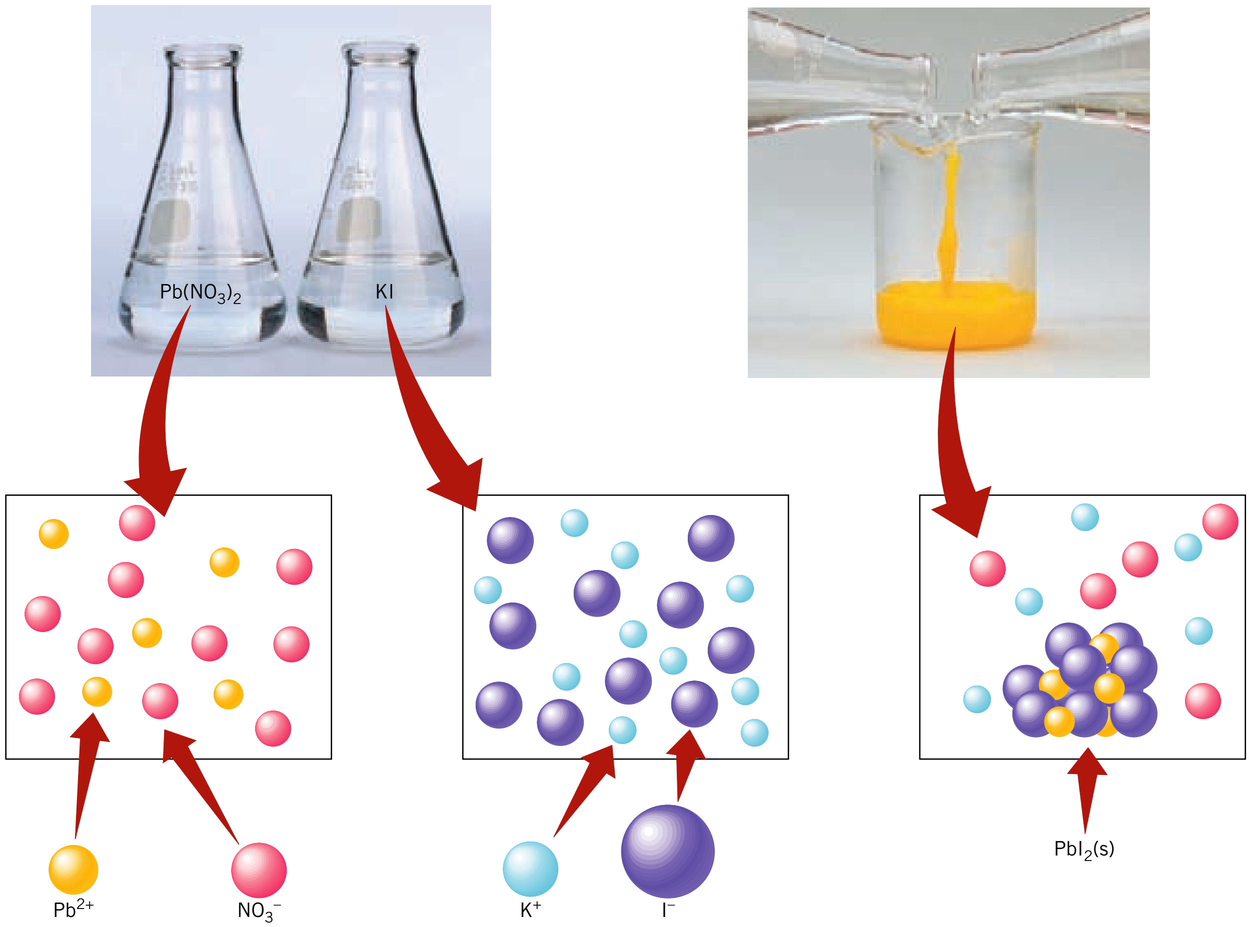


Figure 5.7 | **The reaction of $Pb(NO_3)_2$ with KI.** On the left are flasks containing solutions of lead(II) nitrate and potassium iodide. These solutes exist as separated ions in their respective solutions. On the right, we observe that when the solutions of the ions are combined, there is an immediate reaction as the Pb^{2+} ions join with the I^- ions to give a precipitate of small crystals of solid, yellow PbI_2. The reaction is so rapid that the yellow color develops where the two streams of liquid come together. If the $Pb(NO_3)_2$ and KI are combined in a 1-to-2 mole ratio, the solution surrounding the precipitate would now contain only K^+ and NO_3^- ions (the ions of KNO_3). *(Andy Washnik)*

the substances in solution consist of neutral "molecules." Equation 5.1 is fine for performing stoichiometric calculations, but let's look at other ways we might write the chemical equation.

Soluble ionic compounds are fully dissociated in solution, so $Pb(NO_3)_2$, KI, and KNO_3 are not present in the solution as intact units or "molecules." To show this, we can write the formulas of all soluble strong electrolytes in "dissociated" form to give the **ionic equation** for the reaction.

$$\begin{tikzcd}[column sep=tiny]
& \mathrm{Pb(NO_3)_2}(aq) \arrow[dl] \arrow[dr] & & + & & \mathrm{2KI}(aq) \arrow[dl] \arrow[dr] & & \longrightarrow & \mathrm{PbI_2(s)} & + & & \mathrm{2KNO_3}(aq) \arrow[dl] \arrow[dr] & \\
\mathrm{Pb^{2+}}(aq) & + & \mathrm{2NO_3^-}(aq) & + & \mathrm{2K^+}(aq) & + & \mathrm{2I^-}(aq) & \longrightarrow & \mathrm{PbI_2(s)} & + & \mathrm{2K^+}(aq) & + & \mathrm{2NO_3^-}(aq)
\end{tikzcd}$$

Notice that we have *not* separated PbI_2 into its ions in this equation. This is because PbI_2 has an extremely low solubility in water; it is essentially insoluble. When the Pb^{2+} and I^- ions meet in the solution, insoluble PbI_2 forms and separates as a precipitate. Therefore, after the reaction is over, the Pb^{2+} and I^- ions are no longer able to move independently. They are trapped in the insoluble product.

The ionic equation gives a clearer picture of what is actually going on in the solution during the reaction. The Pb^{2+} and I^- ions come together to form the product. The other ions, K^+ and NO_3^-, are unchanged by the reaction. Ions that do not actually take part in

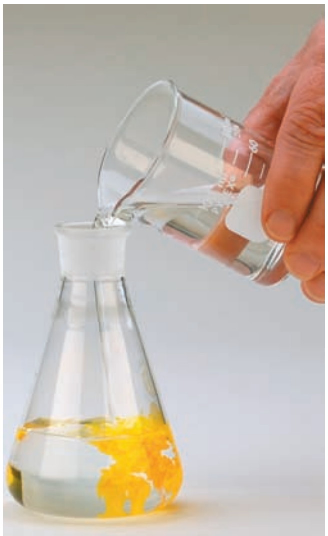


Figure 5.8 | **Another reaction that forms lead iodide.** The net ionic equation tells us that any soluble lead(II) compound will react with any soluble iodide compound to give lead(II) iodide. This prediction is born out here as a precipitate of lead(II) iodide is formed when a solution of sodium iodide is added to a solution of lead(II) acetate. *(Andy Washnik)*

a reaction are sometimes called **spectator ions**; in a sense, they just "stand by and watch the action."

To emphasize the actual reaction that occurs, we can write the **net ionic equation**, which is obtained by eliminating spectator ions from the ionic equation. Let's cross out the spectator ions, K^+ and NO_3^-.

$$Pb^{2+}(aq) + \cancel{2NO_3^-(aq)} + \cancel{2K^+(aq)} + 2I^-(aq) \longrightarrow PbI_2(s) + \cancel{2K^+(aq)} + \cancel{2NO_3^-(aq)}$$

What remains is the net ionic equation,

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

Notice how it calls our attention to the ions that are actually participating in the reaction as well as the change that occurs.

The net ionic equation is especially useful because it permits us to *generalize*. It tells us that if we combine *any* solution that contains Pb^{2+} with *any* other solution that contains I^-, we ought to expect a precipitate of PbI_2. This is exactly what happens if we mix aqueous solutions of lead(II) acetate, $Pb(C_2H_3O_2)_2$, and sodium iodide, NaI. A yellow precipitate of PbI_2 forms immediately (Figure 5.8). Example 5.2 demonstrates how we construct the molecular, ionic, and net ionic equations for the reaction.

Example 5.2
Writing Molecular, Ionic, and Net Ionic Equations

Write the molecular, ionic, and net ionic equations for the reaction of aqueous solutions of lead(II) acetate and sodium iodide, which yields a precipitate of lead(II) iodide and leaves the compound sodium acetate in solution.

■ **Analysis:** Once again, this is a multi-part question. To write the equations, we first need to know the formulas of the reactants and products, so that's the first thing we have to work on. Then we can proceed to construct the three equations to answer the questions.

■ **Assembling the Tools:** The first tool we need to apply is the set of rules of nomenclature you learned in Chapter 3. (If necessary, review them.) These rules tell us the ions involved are: Pb^{2+}, $C_2H_3O_2^-$, Na^+, and I^-. The requirement for electrical neutrality is the next tool we use to obtain the correct formulas of the reactants and products. Then we can use the methods for writing, balancing, and constructing the three kinds of equations asked for in the question.

■ **Solution:** Following the rules we discussed in Chapter 3, we have:

Reactants		**Products**	
lead(II) acetate	$Pb(C_2H_3O_2)_2$	lead(II) iodide	PbI_2
sodium iodide	NaI	sodium acetate	$NaC_2H_3O_2$

The Molecular Equation We assemble the chemical formulas into the molecular equation and balance it.

$$Pb(C_2H_3O_2)_2(aq) + 2NaI(aq) \longrightarrow PbI_2(s) + 2NaC_2H_3O_2(aq)$$

Notice that we've indicated which substances are in solution and which substance is a precipitate. This is the *balanced molecular equation*.

The Ionic Equation To write the ionic equation, we write the formulas of all soluble salts in dissociated form and the formulas of precipitates in "molecular" form. We are careful to use the subscripts and coefficients in the molecular equation to properly obtain the coefficients of the ions in the ionic equation.

$$\overbrace{Pb^{2+}(aq) + 2C_2H_3O_2^-(aq)}^{Pb(C_2H_3O_2)_2} + \overbrace{2Na^+(aq) + 2I^-(aq)}^{2NaI} \longrightarrow PbI_2(s) + \overbrace{2Na^+(aq) + 2C_2H_3O_2^-(aq)}^{2NaC_2H_3O_2}$$

This is the *balanced ionic equation*. Notice that to properly write the ionic equation it is necessary to know both the formulas and charges of the ions.

The Net Ionic Equation We obtain the net ionic equation from the ionic equation by eliminating spectator ions, which are Na^+ and $C_2H_3O_2^-$ (they're the same on both sides of the arrow). Let's cross them out.

$$Pb^{2+}(aq) + \cancel{2C_2H_3O_2^-(aq)} + \cancel{2Na^+(aq)} + 2I^-(aq) \longrightarrow PbI_2(s) + \cancel{2Na^+(aq)} + \cancel{2C_2H_3O_2^-(aq)}$$

What's left is the *net ionic equation*.

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

Notice that this is the same net ionic equation as in the reaction of lead(II) nitrate with potassium iodide.

■ **Are the Answers Reasonable?** When you look back over a problem such as this, things to ask yourself are (1) "Have I written the correct formulas for the reactants and products?" (2) "Is the molecular equation balanced correctly?" (3) "Have I divided the soluble ionic compounds into their ions correctly, being careful to properly apply the subscripts of the ions and the coefficients in the molecular equation?" and (4) "Have I identified and eliminated the correct ions from the ionic equation to obtain the net ionic equation?" If each of these questions can be answered in the affirmative, as they can here, you have solved the problem correctly.

Practice Exercises

5.3 | When solutions of $(NH_4)_2SO_4$ and $Ba(NO_3)_2$ are mixed, a precipitate of $BaSO_4$ forms, leaving soluble NH_4NO_3 in the solution. Write the molecular, ionic, and net ionic equations for the reaction. (*Hint:* Remember that polyatomic ions do not break apart when ionic compounds dissolve in water.)

5.4 | Write molecular, ionic, and net ionic equations for the reaction of aqueous solutions of cadmium chloride and sodium sulfide to give a precipitate of cadmium sulfide and a solution of sodium chloride.

Criteria for Balanced Ionic and Net Ionic Equations

In the ionic and net ionic equations we've written, not only are the atoms in balance, but so is the net electrical charge, which is the same on both sides of the equation. Thus, in the ionic equation for the reaction of lead(II) nitrate with potassium iodide, the sum of the charges of the ions on the left (Pb^{2+}, $2NO_3^-$, $2K^+$, and $2I^-$) is zero, which matches the sum of the charges on all of the formulas of the products (PbI_2, $2K^+$, and $2NO_3^-$).[2] In the net ionic equation the charges on both sides are also the same: on the left we have Pb^{2+} and $2I^-$, with a net charge of zero, and on the right we have PbI_2, also with a charge of zero. We now have an additional requirement for an ionic equation or net ionic equation to be balanced: *the net electrical charge on both sides of the equation must be the same.*

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[2] There is no charge written for the formula of a compound such as PbI_2, so as we add up charges, we take the charge on PbI_2 to be zero.

TOOLS

Criteria for a balanced ionic equation

Criteria for Balanced Ionic and Net Ionic Equations

1. **Material balance.** There must be the same number of atoms of each kind on both sides of the arrow.
2. **Electrical balance.** The *net* electrical charge on the left must equal the *net* electrical charge on the right (although the charge does not necessarily have to be zero).

5.3 | Acids and Bases

Acids and bases constitute a class of compounds that include some of our most familiar chemicals and important laboratory reagents. Many foods, for example, would not be as flavorful if it were not for the tartness imparted by the acids in vinegar or citrus juices. Cola beverages contain an acid that helps give them their unique taste. More powerful acids find uses in cleaning rust from metals and as the liquid in automobile batteries. The white crystals of lye in some drain cleaners, the white substance that makes milk of magnesia opaque, and household ammonia are all bases.

There are some general properties that are common to aqueous solutions of acids and bases. As noted above, foods that contain acids generally have a tart (sour) taste, whereas bases have a somewhat bitter taste and have a soapy "feel." (CAUTION: Taste is ***never*** used as a laboratory test for acids or bases; some are extremely corrosive to animal tissue and some are quite poisonous. ***Never taste any chemicals in the laboratory!***)

Acids and bases also affect the colors of certain dyes we call **acid–base indicators**. An example is litmus (Figure 5.9), which has a pink or red color in an acidic solution and a blue color in a basic solution.[3]

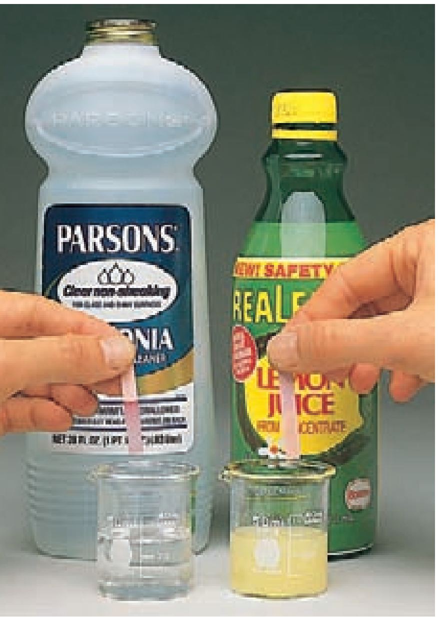

Figure 5.9 | **An acid-base indicator.** Litmus paper, a strip of paper impregnated with the dye litmus, becomes blue in aqueous ammonia (a base) and pink in lemon juice (which contains citric acid). *(Ken Karp)*

■ Acids and bases should be treated with respect because of their potential for causing bodily injury if spilled on the skin. If you spill an acid or base on yourself in the lab, be sure to notify your instructor at once.

■ Even the formula H_3O^+ is something of a simplification. In water the H^+ ion is associated with more than one molecule of water, but we use the formula H_3O^+ as a simple representation.

One of the most important properties of acids and bases is their reaction with each other, a reaction referred to as **neutralization**. For example, when solutions of hydrochloric acid, $HCl(aq)$, and the base sodium hydroxide, $NaOH(aq)$, are mixed the following reaction occurs.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O$$

When the reactants are combined in a 1-to-1 ratio by moles, the acidic and basic properties of the solutes disappear and the resulting solution is neither acidic nor basic. We say an *acid–base neutralization* has occurred. Svante Arrhenius,[4] a Swedish chemist, was the first to suggest that an acid–base neutralization is simply the combination of a hydrogen ion with a hydroxide ion to produce a water molecule, thus making H^+ ions and OH^- ions disappear.

Today we know that in aqueous solutions hydrogen ions, H^+, attach themselves to water molecules to form **hydronium ions**, H_3O^+. When H_3O^+ reacts with something, it gives up a hydrogen ion, so we can think of H^+ as the active ingredient in H_3O^+. Therefore, we often use the term *hydrogen ion* as a substitute for *hydronium ion*, and in many equations, we use $H^+(aq)$ to stand for $H_3O^+(aq)$. Whenever you see the symbol $H^+(aq)$, we are actually referring to $H_3O^+(aq)$.

For most purposes, we find that the following modified versions of Arrhenius' definitions work satisfactorily when we deal with aqueous solutions.

Arrhenius' Definition of Acids and Bases

An **acid** is a substance that reacts with water to produce hydronium ion, H_3O^+.
A **base** is a substance that produces hydroxide ion, OH^-, in water.

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[3] Litmus paper, commonly found among the items in a locker in the general chemistry lab, consists of strips of absorbent paper that have been soaked in a solution of litmus and dried. Red litmus paper is used to test whether a solution is basic. A basic solution turns red litmus blue. To test whether the solution is acidic, blue litmus paper is used. Acidic solutions turn blue litmus red.

[4] Arrhenius proposed his theory of acids and bases in 1884 in his Ph.D. thesis. He won the Nobel Prize for his work in 1903.

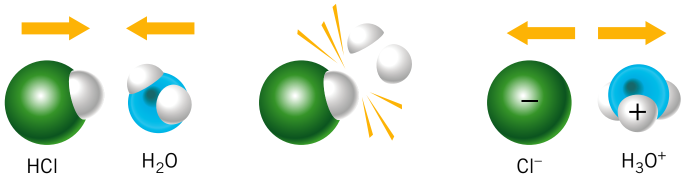

Figure 5.10 | **Ionization of HCl in water.** Collisions between HCl molecules and water molecules lead to a transfer of H^+ from HCl to H_2O, giving Cl^- and H_3O^+ as products.

In general, the reaction of an acid with a base produces an ionic compound as one of the products. In the reaction of HCl(*aq*) with NaOH(*aq*), the compound is sodium chloride, or salt. This reaction is so general, in fact, that *we use the word* **salt** *to mean any ionic compound that doesn't contain either hydroxide ion, OH^-, or oxide ion, O^{2-}.* (Ionic compounds that contain OH^- or O^{2-} are bases, as described below.) Note that we have now slightly modified our definition of the term *salt* given on page 158.

Formation of H_3O^+ by Acids

In general, **acids** are molecular substances that react with water to produce ions, one of which is H_3O^+. For example, when gaseous molecular HCl dissolves in water, a hydrogen ion (H^+) transfers from the HCl molecule to a water molecule. The reaction at the molecular level is depicted in Figure 5.10 using space-filling models,[5] and is represented by the chemical equation

$$HCl(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

This is an **ionization reaction** because ions form where none existed before. Because the solution contains ions, it conducts electricity, so acids are electrolytes.

Sometimes acids also contain hydrogen atoms that are not able to form H_3O^+. An example is ethanoic acid, better known as acetic acid, $HC_2H_3O_2$, the acid that gives vinegar its sour taste. Acetic acid forms H_3O^+ by the following reaction.

$$HC_2H_3O_2(aq) + H_2O \longrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

As a general rule, only the hydrogen written first in the formula transfers to H_2O to give H_3O^+. The structures of the acetic acid molecule and the acetate ion are shown in Figure 5.11, with the hydrogen that can be lost by the acetic acid molecule indicated in the drawing.[6]

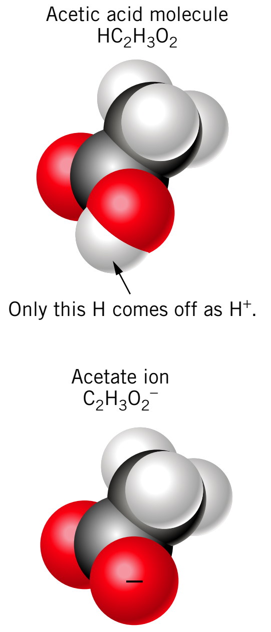

Figure 5.11 | **Acetic acid and acetate ion.** The structures of acetic acid and acetate ion are illustrated here. In acetic acid, only the hydrogen attached to an oxygen can come off as H^+.

As noted earlier, the "active ingredient" in the hydronium ion is H^+, which is why $H^+(aq)$ is often used in place of $H_3O^+(aq)$ in equations. Using this simplification, the ionization of HCl and $HC_2H_3O_2$ in water can be represented as

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

and

$$HC_2H_3O_2(aq) \xrightarrow{H_2O} H^+(aq) + C_2H_3O_2^-(aq)$$

In both reactions, an anion is formed when the acid transfers an H^+ to the water molecule. If we represent the acid molecule by the general formula HA, we can represent the ionization of an acid in general terms by the equation

$$HA + H_2O \longrightarrow H_3O^+ + A^- \tag{5.2}$$

TOOLS

Ionization of an acid in water

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[5] To emphasize the transfer of the H^+, we have shown the positive charge to be on just one of the H atoms in H_3O^+. Actually the charge is distributed evenly over all three H atoms. In effect, the entire H_3O unit carries a single positive charge.

[6] The single negative charge is actually distributed evenly over the two O atoms in the acetate ion.

The molecules HCl and $HC_2H_3O_2$ are capable of furnishing only one H^+ per molecule and are said to be **monoprotic acids. Polyprotic acids** can furnish more than one H^+ per molecule. They undergo reactions similar to those of HCl and $HC_2H_3O_2$, except that the loss of H^+ by the acid occurs in two or more steps. Thus, the ionization of sulfuric acid, a **diprotic acid**, takes place by two successive steps.

$$H_2SO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) + H_2O \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$

Triprotic acids *ionize in three steps*, as illustrated in Example 5.3.

Example 5.3
Writing Equations for Ionization Reactions of Acids

Phosphoric acid, H_3PO_4, is a triprotic acid found in some soft drinks such as Coca-Cola (shown in the photo at the start of this chapter) where it adds a touch of tartness to the beverage. Write equations for its stepwise ionization in water.

Analysis: We are told that H_3PO_4 is a triprotic acid, which is also indicated by the three hydrogens at the beginning of the formula. Because there are three hydrogens to come off the molecule, we expect there to be three steps in the ionization. Each step removes one H^+, and we can use that knowledge to deduce the formulas of the products. Let's line them up so we can see the progression.

$$H_3PO_4 \xrightarrow{-H^+} H_2PO_4^- \xrightarrow{-H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$$

Notice that the loss of H^+ decreases the number of hydrogens by one and increases the negative charge by one unit. Also, the product of one step serves as the reactant in the next step.

Assembling the Tools: We'll use Equation 5.2 for the ionization of an acid as a tool in writing the chemical equation for each step.

Solution: The first step is the reaction of H_3PO_4 with water to give H_3O^+ and $H_2PO_4^-$.

$$H_3PO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + H_2PO_4^-(aq)$$

The second and third steps are similar to the first.

$$H_2PO_4^-(aq) + H_2O \longrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O \longrightarrow H_3O^+(aq) + PO_4^{3-}(aq)$$

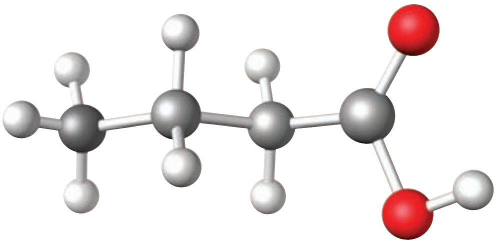
Is the Answer Reasonable? Check to see whether the equations are balanced in terms of atoms and charge. If any mistakes were made, something would be out of balance and we would discover the error. In this case, all of the equations are balanced, so we can feel confident we've written them correctly.

Practice Exercises

5.5 | Write the equation for the ionization of $HCHO_2$ (methanoic acid, commonly called formic acid) in water. Formic acid is used industrially to remove hair from animal skins prior to tanning. (*Hint:* Formic acid and acetic acid are both examples of organic acids.)

5.6 | Butanoic acid, an organic acid with an unpleasant odor found in rancid butter and some fermented cheeses, has the structure shown in the margin. Sketch the structure for the anion formed when butanoic acid is ionized. (*Hint:* Use acetic acid as a guide.) Write the chemical equation for the ionization of butanoic acid in water.

5.7 | Write equations for the stepwise ionization in water of citric acid, $H_3C_6H_5O_7$, the acid in citrus fruits.



Acidity of Nonmetal Oxides

The acids we've discussed so far have been molecules containing hydrogen atoms that can be transferred to water molecules. Nonmetal oxides form another class of compounds that yield acidic solutions in water. Examples are SO_3, CO_2, and N_2O_5 whose aqueous solutions contain H_3O^+ and turn litmus red. These oxides are called **acid anhydrides**, where *anhydride* means "without water." They react with water to form molecular acids containing hydrogen, which are then able to undergo reaction with water to yield H_3O^+.

$$SO_3(g) + H_2O \longrightarrow H_2SO_4(aq) \qquad \text{sulfuric acid}$$

$$N_2O_5(g) + H_2O \longrightarrow 2HNO_3(aq) \qquad \text{nitric acid}$$

$$CO_2(g) + H_2O \longrightarrow H_2CO_3(aq) \qquad \text{carbonic acid}$$

Although carbonic acid is too unstable to be isolated as a pure compound, its solutions in water are quite common. Carbon dioxide from the atmosphere dissolves in rainwater and the waters of lakes and streams where it exists partly as carbonic acid and its ions (i.e., H_3O^+, HCO_3^-, and CO_3^{2-}). This makes these waters naturally slightly acidic. Carbonic acid is also present in carbonated beverages.

Not all nonmetal oxides are acidic anhydrides, just those that are able to react with water. For example, carbon monoxide doesn't react with water, so its solutions in water are not acidic; carbon monoxide, therefore, is not classified as an acidic anhydride.

Formation of OH^- by Bases

Bases fall into two categories: ionic compounds that contain OH^- or O^{2-}, and molecular compounds that react with water to give hydroxide ions. Because solutions of bases contain ions, they conduct electricity. Therefore, bases are electrolytes.

Ionic Hydroxides and Oxides

Ionic bases include metal hydroxides, such as NaOH and $Ca(OH)_2$. When dissolved in water, they dissociate just like other soluble ionic compounds.

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

Soluble metal oxides are **base anhydrides** because they react with water to form the hydroxide ion as one of the products. Calcium oxide is typical.

$$CaO(s) + H_2O \longrightarrow Ca(OH)_2(aq)$$

This reaction occurs when water is added to dry cement or concrete because calcium oxide or "quicklime" is an ingredient in these materials. In this case it is the oxide ion, O^{2-}, that actually forms the OH^-. See Figure 5.12.

$$O^{2-} + H_2O \longrightarrow 2OH^-$$

■ Continued contact of your hands with fresh Portland cement or grout for ceramic tile can lead to irritation because the mixture is quite basic.

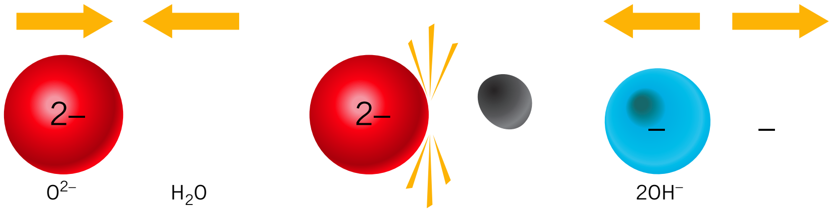


Figure 5.12 | **Oxide ion reacts with water.** When a soluble metal oxide dissolves, the oxide ion takes an H^+ from a water molecule. The result is two hydroxide ions.[7]

Even insoluble metal hydroxides and oxides are bases because they are able to neutralize acids. We will study these reactions in Section 5.5.

Molecular Bases

The most common molecular base is the gas ammonia, NH_3, which dissolves in water and reacts to give a basic solution by the ionization reaction

$$NH_3(aq) + H_2O \longrightarrow NH_4^+(aq) + OH^-(aq)$$

Organic compounds called amines, in which fragments of hydrocarbons replace hydrogen atoms in ammonia, are similar to ammonia in their behavior toward water. An example is methylamine, CH_3NH_2, in which a *methyl group*, CH_3, replaces a hydrogen in ammonia.

$$CH_3NH_2(aq) + H_2O \longrightarrow CH_3NH_3^+(aq) + OH^-(aq)$$

The hydrogen taken from the H_2O molecule becomes attached to the nitrogen atom of the amine. This is how nitrogen-containing bases behave, which is why we've included the H^+ with the other two hydrogens on the nitrogen.

Notice that when a molecular base reacts with water, an H^+ is lost by the water molecule and gained by the base. (See Figure 5.13.) One product is a cation that has one more H and one more positive charge than the reactant base. Loss of H^+ by the water gives the other product, the OH^- ion, which is why the solution is basic. We might represent this by the general equation

$$\text{base} + H_2O \longrightarrow \text{base } H^+ + OH^-$$

If we signify the base by the symbol *B*, this becomes

TOOLS Ionization of a molecular base in water

$$B + H_2O \longrightarrow BH^+ + OH^- \tag{5.3}$$

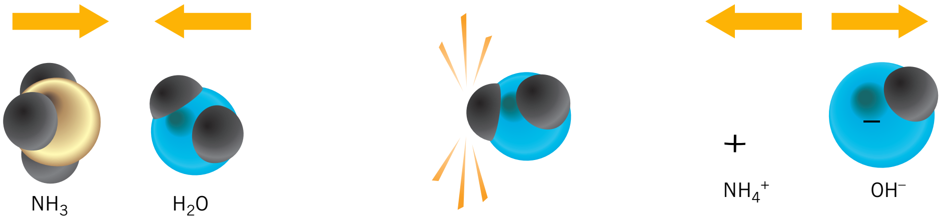


Figure 5.13 | **Ionization of ammonia in water.** Collisions between NH_3 molecules and water molecules lead to a transfer of H^+ from H_2O to NH_3, giving NH_4^+ and OH^- ions.

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[7] You might notice that the sizes of the oxygen atoms in O^{2-}, OH^-, and H_2O are not the same. In Chapter 8 we will discuss how the sizes of atoms change as they gain or lose electrons.

Example 5.4
Writing the Equation for the Ionization of a Molecular Base

Dimethylamine, $(CH_3)_2NH$, is a base in water. It is used commercially as an attractant for boll weevils so they can be destroyed. This insect has caused a more than \$14 billion loss to the yield of cotton in the United States since it arrived from Mexico in 1892. Write an equation for the ionization of $(CH_3)_2NH$ in water.

Analysis: We've been told that $(CH_3)_2NH$ is a base, so it's going to react with water to form hydroxide ion. To write the equation correctly we need to know precisely what the products are. Equation 5.3 is our guide.

Assembling the Tools: The tool is Equation 5.3, which we use as a template for writing the formulas of reactants and products.

Solution: The reactants in the equation are $(CH_3)_2NH$ and H_2O. According to Equation 5.3, when the base reacts with water it takes an H^+ from H_2O, leaving OH^- behind. Therefore, when an H^+ is picked up by $(CH_3)_2NH$, the product will be $(CH_3)_2NH_2^+$. The equation for the reaction is

$$(CH_3)_2NH(aq) + H_2O \longrightarrow (CH_3)_2NH_2^+(aq) + OH^-(aq)$$

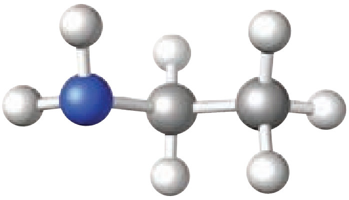
Is the Answer Reasonable? Compare the equation we've written with the general equation for reaction of a base with water. Notice that the formula for the product has one more H and a positive charge, and that the H^+ has been added to the nitrogen. Also, notice that the water has become OH^- when it loses H^+. The equation is therefore correct.

Practice Exercises

5.8 | Triethylamine, $(C_2H_5)_3N$, is a base in water. Write an equation for its reaction with the solvent. (*Hint:* How do nitrogen-containing bases react toward water?)

5.9 | Hydroxylamine, $HONH_2$, is a molecular base in water. Write an equation for its reaction with the solvent.

5.10 | Ethylamine, a base in water, has the following structure:



It is used in the manufacture of many herbicides. Sketch the structure of the nitrogen-containing product that is formed when it reacts with water. Write the equation for the ionization of ethylamine in water.

Strong and Weak Acids and Bases

Ionic compounds such as NaCl and $CaCl_2$ break up essentially 100% into ions in water. No "molecules" or formula units of either NaCl or $CaCl_2$ are detectable in their aqueous solutions. Because these solutions contain so many ions, they are strong conductors of electricity, so ionic compounds are said to be **strong electrolytes.**

All strong acids are strong electrolytes.

Hydrochloric acid is also a strong electrolyte. Its ionization in water is essentially complete; its solutions are strongly acidic, and it is said to be a *strong acid.* In general, acids that are strong electrolytes are called **strong acids**. There are relatively few strong acids; the most common ones are as follows:

List of strong acids

Strong Acids	
$HClO_4(aq)$	perchloric acid
$HClO_3(aq)$	chloric acid
$HCl(aq)$	hydrochloric acid
$HBr(aq)$	hydrobromic acid
$HI(aq)$	hydroiodic acid[8]
$HNO_3(aq)$	nitric acid
$H_2SO_4(aq)$	sulfuric acid

Metal hydroxides are ionic compounds, so they are also strong electrolytes. Those that are soluble are the hydroxides of Group 1A and the hydroxides of calcium, strontium, and barium of Group 2A. Solutions of these compounds are strongly basic, so these substances are considered to be **strong bases.** The hydroxides of other metals have very low solubilities in water. They are strong electrolytes in the sense that the small amounts of them that dissolve in solution are completely dissociated. However, because of their low solubility in water, their solutions are very weakly basic.

Weak Acids and Bases: Weak Electrolytes

Most acids are not completely ionized in water. For instance, a solution of acetic acid, $HC_2H_3O_2$, is a relatively poor conductor of electricity compared to a solution of HCl with the same concentration (Figure 5.14). An acid, such as acetic acid, that is not fully ionized in water is classified as a **weak electrolyte** and is a **weak acid.**

An acetic acid solution is a poor conductor because in the solution only a small fraction of the acid exists as H_3O^+ and $C_2H_3O_2^-$ ions. The rest is present as molecules of $HC_2H_3O_2$. This is because $C_2H_3O_2^-$ ions have a strong tendency to react with H_3O^+ when the ions meet in the solution. As a result, there are two opposing reactions occurring simultaneously (Figure 5.15). One reaction forms the ions,

$$HC_2H_3O_2(aq) + H_2O \longrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

and the other removes ions,

$$H_3O^+(aq) + C_2H_3O_2^-(aq) \longrightarrow HC_2H_3O_2(aq) + H_2O$$

A balance is reached when ions form and disappear at the same rate, and for acetic acid this happens when only a small percentage of the $HC_2H_3O_2$ is ionized.

The condition we've just described, with two opposing reactions occurring at the same rate, is called a **chemical equilibrium** or **dynamic equilibrium.** It is an *equilibrium* because the concentrations of the substances present in the solution do not change with time; it is *dynamic* because the opposing reactions continue endlessly.

The two opposing processes in a dynamic equilibrium are usually represented in a single equation by using double arrows, $\rightleftharpoons$. For acetic acid, we write

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

The **forward reaction** (read from left to right) forms the ions; the **reverse reaction** (from right to left) removes them from the solution.

Molecular bases, such as ammonia and methylamine, are also weak electrolytes and have a low percentage ionization; they are classified as **weak bases**. See Figure 5.14*c*. In a solution of ammonia, only a small fraction of the solute is ionized to give NH_4^+ and OH^- because the ions have a strong tendency to react with each other. This leads to the dynamic equilibrium (Figure 5.16)

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

in which most of the base is present as NH_3 molecules.

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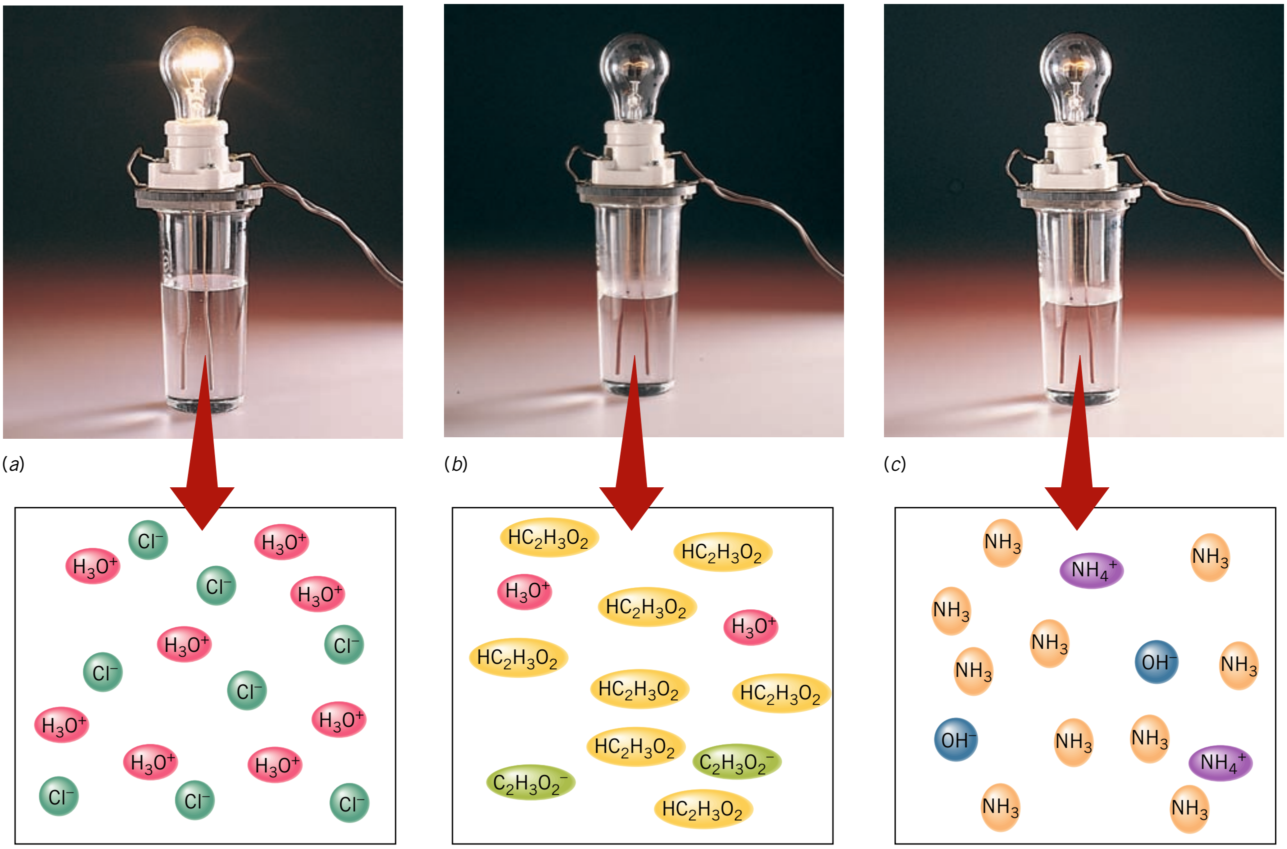
[8] Sometimes the first "o" in the name of $HI(aq)$ is dropped for ease of pronunciation to give *hydriodic acid*.

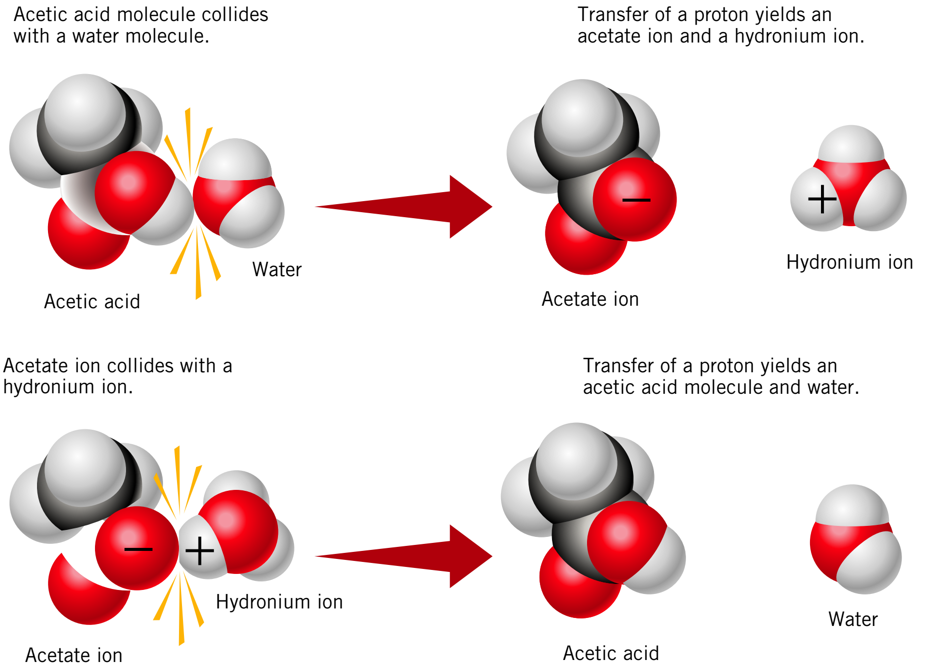


All the HCl is ionized in the solution, so there are many ions present.

Only a small fraction of the acetic acid is ionized, so there are few ions to conduct electricity. Most of the acetic acid is present as neutral molecules of $HC_2H_3O_2$.

Only a small fraction of the ammonia is ionized, so few ions are present to conduct electricity. Most of the ammonia is present as neutral molecules of NH_3.

Figure 5.14 | **Electrical conductivity of solutions of strong and weak acids and bases at equal concentrations.** (*a*) HCl is 100% ionized and is a strong conductor, enabling the light to glow brightly. (*b*) $HC_2H_3O_2$ is a weaker conductor than HCl because the extent of its ionization is far less, so the light is dimmer. (*c*) NH_3 also is a weaker conductor than HCl because the extent of its ionization is low, and the light remains dim. *(Michael Watson)*


Acetic acid molecule collides with a water molecule.

Transfer of a proton yields an acetate ion and a hydronium ion.

Acetate ion collides with a hydronium ion.

Transfer of a proton yields an acetic acid molecule and water.

Figure 5.15 | **Equilibrium in a solution of acetic acid.** Two opposing reactions take place simultaneously in a solution of acetic acid. Molecules of acid collide with molecules of water and form acetate ions and H_3O^+ ions. Meanwhile, acetate ions collide with H_3O^+ ions to give acetic acid molecules and water molecules.

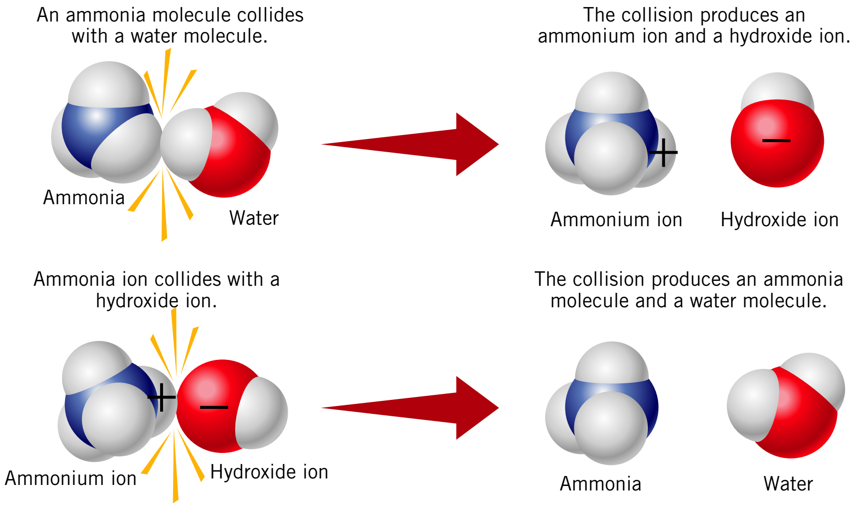

An ammonia molecule collides with a water molecule.
Ammonia
Water
The collision produces an ammonium ion and a hydroxide ion.
+
−
Ammonium ion
Hydroxide ion
Ammonia ion collides with a hydroxide ion.
+
−
Ammonium ion
Hydroxide ion
The collision produces an ammonia molecule and a water molecule.
Ammonia
Water

Figure 5.16 | **Equilibrium in a solution of the weak base ammonia.** Collisions between water and ammonia molecules produce ammonium and hydroxide ions. The reverse process, which involves collisions between ammonium ions and hydroxide ions, removes ions from the solution and forms ammonia and water molecules.

Let's briefly summarize the results of our discussion.

Weak acids and bases are weak electrolytes.
Strong acids and bases are strong electrolytes.

In describing equilibria such as those above, we will often talk about the **position of equilibrium**, which is the extent to which the forward reaction proceeds toward completion. If very little of the products are present at equilibrium, the forward reaction has not gone far toward completion and we say "the position of equilibrium lies to the left," toward the reactants. On the other hand, if large amounts of the products are present at equilibrium, we say "the position of equilibrium lies to the right."

For any weak electrolyte, when equilibrium is reached only a small percentage of the solute is actually ionized, so the position of equilibrium lies to the left. To call acetic acid a *weak* acid, for example, is just another way of saying that the forward reaction in the equilibrium is far from completion. It is also important to understand that calling acetic acid a weak acid does not imply a small concentration of $HC_2H_3O_2$. Rather, the concentration of H_3O^+ is small because only a small fraction of the solute is ionized. Even a concentrated solution of $HC_2H_3O_2$ is weakly acidic.

Complete Ionization of Strong Acids

With strong electrolytes such as HCl, the tendency of the forward ionization reaction to occur is very large, while the tendency of the reverse reaction to occur is extremely small. As a result, all of the HCl molecules dissolved in water become converted to H_3O^+ and Cl^- ions; the acid becomes 100% ionized. For this reason, *we do not use double arrows in describing what happens when HCl(g) or any other strong electrolyte undergoes ionization or dissociation.*

Practice Exercises

5.11 | Earlier you learned that methylamine, CH_3NH_2 (a fishy-smelling substance found in herring brine), is a base in water. Write the equation that shows that methylamine is a weak base. (Hint: How do we show that an equilibrium exists in the solution?)

5.12 | Nitrous acid, HNO_2, is a weak acid thought to be responsible for certain cancers of the intestinal system. Write the chemical equation that shows that HNO_2 is a weak acid in water.

5.4 | Acid-Base Nomenclature

Although at first there seems to be little order in the naming of acids, there are patterns that help organize names of acids and the anions that come from them when the acids are neutralized.

Hydrogen Compounds of Nonmetals

The binary compounds of hydrogen with many of the nonmetals are acidic, and in their aqueous solutions they are referred to as **binary acids**. Some examples are HCl, HBr, and H_2S. In naming these substances as acids, we add the prefix *hydro-* and the suffix *-ic* to the stem of the nonmetal name, followed by the word *acid.* For example, aqueous solutions of hydrogen chloride and hydrogen sulfide are named as follows:

Name of the molecular compound		Name of the binary acid in water	
$HCl(g)$	hydrogen chloride	$HCl(aq)$	*hydro*chlor*ic acid*
$H_2S(g)$	hydrogen sulfide	$H_2S(aq)$	*hydro*sulfur*ic acid*

■ In the name of an acid, the prefix *hydro-* tells us it is a binary acid. If the prefix *hydro-* is absent, it tells us the substance is not a binary acid.

Notice that the gaseous molecular substances are named in the usual way as binary compounds. *It is their aqueous solutions that are named as acids.*

When an acid is neutralized, the salt that is produced contains the anion formed by removing a hydrogen ion, H^+, from the acid molecule. Thus HCl yields salts containing the chloride ion, Cl^-. Similarly, HBr gives salts containing the bromide ion, Br^-. In general, then, neutralization of a binary acid yields the simple anion of the nonmetal.

Naming Oxoacids

Acids that contain hydrogen, oxygen, plus another element are called **oxoacids**. Examples are H_2SO_4 and HNO_3. These acids do not take the prefix *hydro-*. Many nonmetals form two or more oxoacids that differ in the number of oxygen atoms in their formulas. When there are two oxoacids, the one with the larger number of oxygens takes the suffix *-ic* and the one with the fewer number of oxygens takes the suffix *-ous*.

H_2SO_4	sulfur*ic acid*	HNO_3	nitr*ic acid*
H_2SO_3	sulfur*ous acid*	HNO_2	nitr*ous acid*

The halogens can form as many as four different oxoacids. The oxoacid with the most oxygens has the prefix *per-,* and the one with the least has the prefix *hypo-*.

$HClO$	*hypo*chlor*ous acid* (usually written HOCl)	$HClO_3$	chlor*ic acid*
$HClO_2$	chlor*ous acid*	$HClO_4$	*per*chlor*ic acid*

The neutralization of oxoacids produces negative polyatomic ions. The name of the polyatomic ion is related to that of its parent acid.

(1) *-ic* acids give *-ate* anions: HNO_3 (nitr*ic acid*) $\longrightarrow$ NO_3^- (nitr*ate* ion)

(2) *-ous* acids give *-ite* anions: H_2SO_3 (sulfur*ous acid*) $\longrightarrow$ SO_3^{2-} (sulf*ite* ion)

Acid and anion names

This relationship between the name of the acid and name of the anion carries over to other acids that end in the suffix *-ic*. For example, acetic acid gives the anion acetate, and citric acid gives the anion citrate.

In naming polyatomic anions, the prefixes *per-* and *hypo-* carry over from the name of the parent acid. Thus perchloric acid, $HClO_4$, gives perchlorate ion, ClO_4^-, and hypochlorous acid, HClO, gives hypochlorite ion, ClO^-.

Knowing the names and formulas of the polyatomic ions in Table 3.5 will help you in naming the acids as well. For example, the thiocyanate ion, SCN^-, has a name that ends in *-ate*. The anion is derived by removing an H^+ from an acid with a name that ends in *-ic*. Therefore, thiocyan*ate* ion, SCN^-, comes from thiocyan*ic* acid, HSCN.

Example 5.5
Naming Acids and Their Salts

Bromine forms four oxoacids, similar to those of chlorine. What is the name of the acid $HBrO_2$ and what is the name of the salt $NaBrO_3$?

Analysis: In this problem we will reason by analogy and begin by analyzing the names of the acids of the halogens. Then we can apply the nomenclature rules above to deduce the answers.

Assembling the Tools: There are two tools we can use here: (1) how names are related to the number of oxygens in the acid, and (2) how the ending on the name of the anion relates to the ending on the name of the acid.

Solution:

Naming $HBrO_2$: The oxoacids of chlorine are

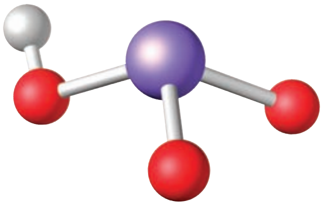
HClO	hypochlorous acid	$HClO_3$	chloric acid
$HClO_2$	chlorous acid	$HClO_4$	perchloric acid

The acid $HBrO_2$ is similar to chlorous acid, so to name it we will use the stem of the element name bromine (brom-) in place of chlor-. Therefore, the name of $HBrO_2$ is *bromous acid.*

Naming $NaBrO_3$: $NaBrO_3$ is a salt that would form by neutralization of an acid with the formula $HBrO_3$ (the H^+ of the acid is replaced by Na^+). This acid has one more oxygen than bromous acid, $HBrO_2$, so its name would have the ending *-ic*. This means $HBrO_3$ is bromic acid. Neutralizing an acid that has a name that ends in *-ic* gives an anion with a name that ends in *-ate*, so the anion BrO_3^- is the bromate ion. Therefore, the salt $NaBrO_3$ is *sodium bromate.*

Are the Answers Reasonable? There's really not much we can do to check the answers here. For the salt, if $HClO_3$ is chloric acid, then it seems reasonable that $HBrO_3$ would be bromic acid, which would mean that BrO_3^- is the bromate ion and $NaBrO_3$ is sodium bromate. Alternatively, if you remember the polyatomic ions from Chapter 3, you know that ClO_3^- is the chlorate ion. By analogy, BrO_3^- would be bromate ion, so $NaBrO_3$ is sodium bromate.

Practice Exercises



5.13 | The formula for arsenic acid is H_3AsO_4. What is the name of the salt Na_3AsO_4? (*Hint:* Recall how the name of the anion is related to the name of the acid.)

5.14 | Methanoic acid is also called formic acid and has the formula $HCHO_2$. What are two names for the salt $Ca(CHO_2)_2$?

5.15 | Name the water solutions of the following acids: HF, HBr. Name the sodium salts formed by neutralizing these acids with NaOH.

5.16 | What is the name of the acid having the structure shown in the margin? (Use the colors of the atoms to identify the elements in the acid.)

Acid Salts

If a polyprotic acid is neutralized stepwise, the neutralization can be halted before all the hydrogens have been removed. For example, partial neutralization of H_2SO_4 gives the HSO_4^- ion, which forms salts such as $NaHSO_4$. This compound is called an **acid salt** because its anion, HSO_4^-, is capable of furnishing additional H^+.

In naming ions such as HSO_4^-, we specify the number of hydrogens that can still be neutralized if the anion were to be treated with additional base. Thus, HSO_4^- is called the hydrogen sulfate ion; it's the active ingredient in Sani-Flush (Figure 5.17). Similarly, $H_2PO_4^-$ is the dihydrogen phosphate ion. These two anions give the following salts with Na^+:

$NaHSO_4$	sodium hydrogen sulfate
NaH_2PO_4	sodium dihydrogen phosphate

For acid salts of diprotic acids, the prefix ***bi-*** is still often used.

$NaHCO_3$	sodium bicarbonate or sodium hydrogen carbonate

Notice that the prefix bi- does *not* mean "two"; instead, it means that there is an acidic hydrogen in the compound.

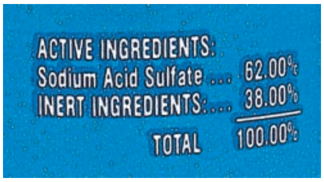

ACTIVE INGREDIENTS:
Sodium Acid Sulfate ... 62.00%
INERT INGREDIENTS: ... 38.00%
TOTAL 100.00%

Figure 5.17 | **Applications of acid salts.** The label on a can of Sani-Flush shows the active ingredient to be sodium hydrogen sulfate, which the manufacturer calls "sodium acid sulfate." *(Robert Capece)*

Practice Exercises

5.17 | What is the formula for sodium bisulfite? What is the chemically correct name for this compound? (*Hint:* What information do we get from the prefix bi- and the suffix -ite?)

5.18 | Write molecular equations for the stepwise neutralization of phosphoric acid by sodium hydroxide. What are the names of the salts that are formed?

Naming Bases

Metal compounds that contain the ions OH^- or O^{2-}, such as NaOH and Na_2O, are ionic and are named just like any other ionic compound. Thus, NaOH is sodium hydroxide and Na_2O is sodium oxide.

Molecular bases such as NH_3 (ammonia) and CH_3NH_2 (methylamine) are specified by just giving the name of the molecule.[9] There is nothing in their names that specifically tells us they are bases.

■ Knowing that methylamine is a base requires that you know that amines in general are bases.

5.5 | Double Replacement (Metathesis) Reactions

In our discussion of the reaction of KI with $Pb(NO_3)_2$, you saw that the net ionic equation reveals a change in the number of ions in solution when the reaction takes place. Such changes characterize ionic reactions in general. In this section you will learn how we can use the existence or nonexistence of a net ionic equation as a criterion to determine whether or not an ionic reaction occurs in a solution of mixed solutes.

> In general, a net ionic equation will exist (and a reaction will occur) under the following conditions:
>
> A precipitate is formed from a mixture of soluble reactants.
> An acid reacts with a base.
> A weak electrolyte is formed from a mixture of strong electrolytes.
> A gas is formed from a mixture of reactants.

TOOLS

Predicting net ionic equations

It is also important to note that *no net reaction will occur if all of the substances in the ionic equation cancel.* There will be no net ionic equation, and therefore no net reaction!

■ If all the ions are spectator ions, there is no net reaction.

Predicting Precipitation Reactions

The reaction between $Pb(NO_3)_2$ and KI,

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

---

[9] Solutions of ammonia in water are sometimes called *ammonium hydroxide*, although there is no evidence that the species NH_4OH actually exists.

TOOLS

Solubility rules

Table 5.1 Solubility Rules for Ionic Compounds in Water

Soluble Compounds

1. All componds of the alkali metals (Group 1A) are soluble.
2. All salts containng NH_4^+, NO_3^-, ClO_4^-, ClO_3^-, and $C_2H_3O_2^-$ are soluble.
3. All chlorides, bromides, and iodides (salts containing Cl^-, Br^-, or I^-) are soluble *except* when combined with Ag^+, Pb^{2+}, and Hg_2^{2+} (note the subscript 2).
4. All sulfates (salts containing SO_4^{2-}) are soluble *except* those of Pb^{2+}, Ca^{2+}, Sr^{2+}, Hg_2^{2+}, and Ba^{2+}.

Insoluble Compounds

5. All metal hydroxides (ionic compounds containing OH^-) and all metal oxides (ionic compounds containing O^{2-}) are insoluble *except* those of Group 1A and those of Ca^{2+}, Sr^{2+}, and Ba^{2+}.

   When metal oxides do dissolve, they react with water to form hydroxides. The oxide ion, O^{2-}, does not exist in water. For example:

$$Na_2O(s) + H_2O \longrightarrow 2NaOH(aq)$$

6. All salts that contain PO_4^{3-}, CO_3^{2-}, SO_3^{2-}, and S^{2-} are insoluble, *except* those of Group 1A and NH_4^+.

is just one example of a large class of ionic reactions, called **metathesis reactions**, in which cations and anions change partners. Metathesis reactions are also sometimes called **double replacement reactions.** (In the formation of the products, PbI_2 and KNO_3, the I^- replaces NO_3^- in the lead compound and NO_3^- replaces I^- in the potassium compound.) Metathesis reactions in which a precipitate forms are also called **precipitation reactions.**

Lead(II) nitrate and potassium iodide react because one of the products is insoluble. Such reactions can be predicted if we know which substances are soluble and which are insoluble. To help us, we can apply a set of **solubility rules** (Table 5.1) that tell us, in many cases, whether an ionic compound is soluble or insoluble. To make the rules easier to remember, they are divided into two categories. The first includes compounds that are soluble, with some exceptions. The second describes compounds that are generally insoluble, with some exceptions. Some examples will help clarify their use.

Rule 1 states that all compounds of the alkali metals are soluble in water. This means that you can expect *any* compound containing Na^+ or K^+, or any of the Group 1A metal ions, *regardless of the anion*, to be soluble. If one of the reactants in a metathesis is Na_3PO_4, you now know from Rule 1 that it is soluble. Therefore, you would write it in *dissociated* form in the ionic equation. Similarly, Rule 6 states, in part, that all carbonate compounds are *insoluble* except those of the alkali metals and the ammonium ion. If one of the products in a metathesis reaction is $CaCO_3$, you'd expect it to be insoluble because the cation is not an alkali metal or NH_4^+. Therefore, you would write its formula in the *undissociated* form as $CaCO_3(s)$ in the ionic equation.

Example 5.6 illustrates how we can use the rules to predict the outcome of a reaction.

Example 5.6
Predicting Reactions and Writing Their Equations

Predict whether a reaction will occur when aqueous solutions of $Pb(NO_3)_2$ and $Fe_2(SO_4)_3$ are mixed. Write molecular, ionic, and net ionic equations for it.

■ **Analysis:** For the molecular equation, let's start by writing the reactants on the left.

$$Pb(NO_3)_2 + Fe_2(SO_4)_3 \longrightarrow$$

To complete the equation we have to determine the makeup of the products. We begin, therefore, by predicting what a double replacement (metathesis) might produce. Next, we proceed to construct the ionic equation, and then convert it to a net ionic equation by crossing out spectator ions. If a net ionic equation exists at this point, it tells us that a reaction does indeed take place.

The critical link in determining whether a reaction occurs is obtaining a net ionic equation.

Assembling the Tools: The tools you've learned that apply here are (1) rules for writing the formula of a salt from the formulas of its ions, (2) the rules for writing ionic and net ionic equations, and (3) the solubility rules.

Solution: The reactants, $Pb(NO_3)_2$ and $Fe_2(SO_4)_3$, contain the ions Pb^{2+} and NO_3^-, and Fe^{3+} and SO_4^{2-}, respectively. To write the formulas of the products, we interchange anions, being careful to require that the formula units be electrically neutral. This gives $PbSO_4$ as one possible product and $Fe(NO_3)_3$ as the other. The unbalanced molecular equation at this point is

$$Pb(NO_3)_2 + Fe_2(SO_4)_3 \longrightarrow PbSO_4 + Fe(NO_3)_3 \quad \text{(unbalanced)}$$

Next, let's determine solubilities. The reactants are ionic compounds and we are told that they are in solution, so we know they are water soluble. Solubility Rules 2 and 4 tell us this also. For the products, we find that Rule 2 says that all nitrates are soluble, so $Fe(NO_3)_3$ is soluble; Rule 4 tells us that the sulfate of Pb^{2+} is *insoluble*. This means that a precipitate of $PbSO_4$ will form. Writing (*aq*) and (*s*) following appropriate formulas, the unbalanced molecular equation is

$$Fe_2(SO_4)_3(aq) + Pb(NO_3)_2(aq) \longrightarrow Fe(NO_3)_3(aq) + PbSO_4(s) \quad \text{(unbalanced)}$$

Always write equations in two steps. First write correct formulas for the reactants and products, then adjust the coefficients to balance the equation.

When balanced, we obtain the *molecular equation*.

$$Fe_2(SO_4)_3(aq) + 3Pb(NO_3)_2(aq) \longrightarrow 2Fe(NO_3)_3(aq) + 3PbSO_4(s)$$

Next, we expand this to give the *ionic equation* in which soluble compounds are written in dissociated (separated) form as ions, and insoluble compounds are written in "molecular" form. Once again, we are careful to apply the subscripts of the ions and the coefficients.

$$2Fe^{3+}(aq) + 3SO_4^{2-}(aq) + 3Pb^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 2Fe^{3+}(aq) + 6NO_3^-(aq) + 3PbSO_4(s)$$

By removing spectator ions (Fe^{3+} and NO_3^-), we obtain

$$3Pb^{2+}(aq) + 3SO_4^{2-}(aq) \longrightarrow 3PbSO_4(s)$$

Finally, we reduce the coefficients to give us the correct *net ionic equation.*

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

The existence of the net ionic equation confirms that a reaction does take place between lead(II) nitrate and iron(III) sulfate.

Is the Answer Reasonable? One of the main things we have to check in solving a problem such as this is that we've written the correct formulas of the products. For example, in this problem some students might be tempted (without thinking) to write $Pb(SO_4)_2$ and $Fe_2(NO_3)_3$, or even $Pb(SO_4)_3$ and $Fe_2(NO_3)_2$. *This is a common error.* Always be careful to figure out the charges on the ions that must be combined in the formula. Then take the ions in a ratio that gives an electrically neutral formula unit.

Once we're sure the formulas of the products are right, we check that we've applied the solubility rules correctly, which we have. Then we check that we've properly balanced the equation (We have.), that we've correctly divided the soluble compounds into their ions (We have.), and that we've eliminated the spectator ions to obtain the net ionic equation (We have.).

Practice Exercises

5.19 | Show that in aqueous solutions there is no net reaction between $Zn(NO_3)_2$ and $Ca(C_2H_3O_2)_2$. (*Hint:* Write molecular, ionic, and net ionic equations.)

5.20 | Predict the reaction that occurs on mixing the following solutions. Write molecular, ionic, and net ionic equations for the reactions that take place. (a) $AgNO_3$ and NH_4Cl, (b) sodium sulfide and lead(II) acetate.

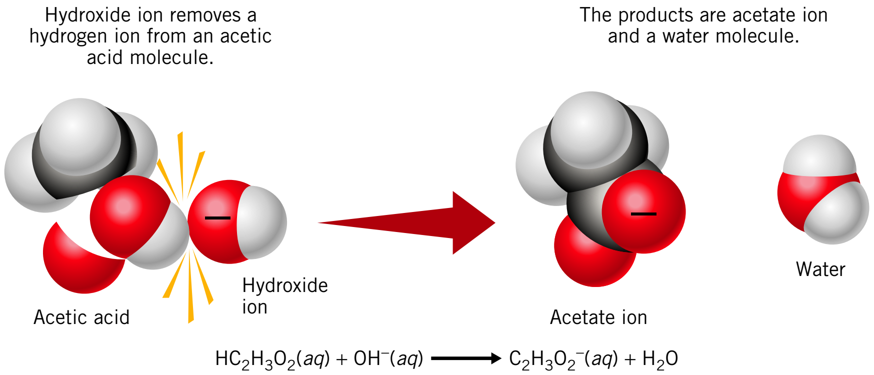

Hydroxide ion removes a hydrogen ion from an acetic acid molecule.
The products are acetate ion and a water molecule.
Acetic acid
Hydroxide ion
Acetate ion
Water
$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$

Figure 5.18 | **Net reaction of acetic acid with a strong base.** The neutralization of acetic acid by hydroxide ion occurs primarily by the removal of H^+ from acetic acid molecules by OH^- ions.

Predicting Acid–Base Reactions

Recall from Section 5.3 that neutralization is one of the key properties of acids and bases. Many such reactions can be viewed as metathesis. An example is the reaction between HCl and NaOH.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O$$

Writing this as an ionic equation gives

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O$$

where we have used H^+ as shorthand for H_3O^+. The net ionic equation is obtained by removing spectator ions.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

In this case, a net ionic equation exists because of the formation of a very weak electrolyte, H_2O, instead of a precipitate. In fact, we find this same net ionic equation for any reaction between a strong acid and a soluble strong base.

The formation of water in a neutralization reaction is such a strong driving force for reaction that it will form even if the acid is weak or if the base is insoluble, or both. Here are some examples.

Reaction of a Weak Acid with a Strong Base

Molecular equation:

$$\underset{\text{weak acid}}{HC_2H_3O_2(aq)} + \underset{\text{strong base}}{NaOH(aq)} \longrightarrow NaC_2H_3O_2(aq) + H_2O$$

Net ionic equation:

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$$

This reaction is illustrated in Figure 5.18.

Reaction of a Strong Acid with an Insoluble Base

Figure 5.19 shows the reaction of hydrochloric acid with milk of magnesia, which contains $Mg(OH)_2$.

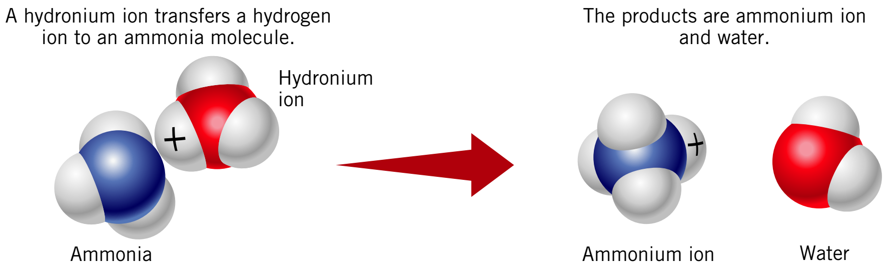
Molecular equation:

$$\underset{\text{strong acid}}{2HCl(aq)} + \underset{\text{insoluble base}}{Mg(OH)_2(s)} \longrightarrow MgCl_2(aq) + 2H_2O$$

Net ionic equation:

$$2H^+(aq) + Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2H_2O$$

Figure 5.19 | **Hydrochloric acid is neutralized by milk of magnesia.** A solution of hydrochloric acid is added to a beaker containing milk of magnesia. The thick white solid in milk of magnesia is magnesium hydroxide, $Mg(OH)_2$, which is able to neutralize the acid. The mixture is clear where some of the solid $Mg(OH)_2$ has already reacted and dissolved. *(Andy Washnik)*


A hydronium ion transfers a hydrogen ion to an ammonia molecule.
Hydronium ion
+
Ammonia
The products are ammonium ion and water.
+
Ammonium ion
Water

$$NH_3(aq) + H_3O^+(aq) \longrightarrow NH_4^+(aq) + H_2O$$

Figure 5.20 | **Reaction of ammonia with a strong acid.** The reaction occurs primarily by the direct attack of H_3O^+ on NH_3 molecules. Transfer of a proton to the ammonia molecule produces an ammonium ion and a water molecule.

Reaction of a Weak Acid with an Insoluble Base

Molecular equation:

$$\underset{\text{weak acid}}{2HC_2H_3O_2(aq)} + \underset{\text{insoluble base}}{Mg(OH)_2(s)} \longrightarrow Mg(C_2H_3O_2)_2(aq) + 2H_2O$$

Net ionic equation:

$$2HC_2H_3O_2(aq) + Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2C_2H_3O_2^-(aq) + 2H_2O$$

Notice that in the last two examples, the formation of water drives the reaction, even though one of the reactants is insoluble. To correctly write the ionic and net ionic equations, it is important to know both the solubility rules and which acids are strong and weak. If you've learned the list of strong acids, you can expect that any acid *not* on the list will be a weak acid. (Unless specifically told otherwise, you should assume weak acids to be water soluble.)

Reaction of an Acid with a Weak Base

Acid–base neutralization doesn't always involve the formation of water. We see this in the reaction of an acid with a weak base such as NH_3. For a strong acid such as HCl, we have

Molecular equation:

$$HCl(aq) + NH_3(aq) \longrightarrow NH_4Cl(aq)$$

Net ionic equation (using H^+ as shorthand for H_3O^+):

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

Figure 5.20 depicts the transfer of H^+ from H_3O^+ to NH_3.

With a weak acid such as $HC_2H_3O_2$, we have

Molecular equation:

$$HC_2H_3O_2(aq) + NH_3(aq) \longrightarrow NH_4C_2H_3O_2(aq)$$

Ionic and net ionic equation:

$$HC_2H_3O_2(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) + C_2H_3O_2^-(aq)$$

Even though solutions of $HC_2H_3O_2$ contain some H^+, and solutions of NH_3 contain some OH^-, when these solutions are mixed the predominant reaction is between molecules of acid and base. This is illustrated in Figure 5.21.

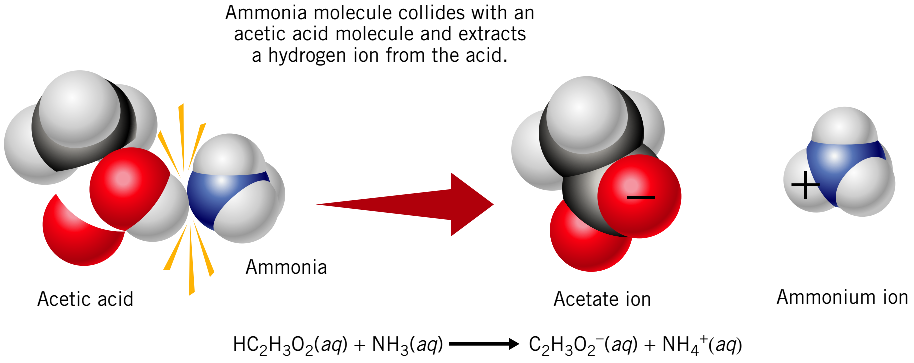
Practice Exercises

5.21 | Write the molecular, ionic, and net ionic equations for the neutralization of $HNO_3(aq)$ by $Ca(OH)_2(aq)$. (*Hint:* First determine whether the acid and base are strong or weak.)

5.22 | Write molecular, ionic, and net ionic equations for the reaction of (a) HCl with KOH, (b) $HCHO_2$ with LiOH, and (c) N_2H_4 with HCl.

5.23 | Write molecular, ionic, and net ionic equations for the reaction of the weak base methylamine, CH_3NH_2, with formic acid, $HCHO_2$ (a weak acid).

Figure 5.21 | **Reaction of acetic acid with ammonia.** The collision of an ammonia molecule with an acetic acid molecule leads to a transfer of H^+ from the acetic acid to ammonia and the formation of ions.


Ammonia molecule collides with an acetic acid molecule and extracts a hydrogen ion from the acid.
Acetic acid
Ammonia
Acetate ion
Ammonium ion
−
+
$HC_2H_3O_2(aq) + NH_3(aq) \longrightarrow C_2H_3O_2^-(aq) + NH_4^+(aq)$

Predicting Reactions in Which a Gas Is Formed

Sometimes a product of a metathesis reaction is a substance that normally is a gas at room temperature and is not very soluble in water. The most common example is carbon dioxide. This product forms when an acid reacts with either a bicarbonate or carbonate. For example, as a sodium bicarbonate solution is added to hydrochloric acid, bubbles of carbon dioxide are released (Figure 5.22). This is the same reaction that occurs if you take sodium bicarbonate to soothe an upset stomach. Stomach acid is HCl and its reaction with the $NaHCO_3$ both neutralizes the acid and produces CO_2 gas (burp!). The molecular equation for the metathesis reaction is

Figure 5.22 | **The reaction of sodium bicarbonate with hydrochloric acid.** The bubbles contain the gas carbon dioxide. *(Michael Watson)*

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2CO_3(aq)$$

Carbonic acid, H_2CO_3, is too unstable to be isolated in pure form. When it forms in appreciable amounts as a product in a metathesis reaction, it decomposes into its anhydride, CO_2, and water. Carbon dioxide is only slightly soluble in water, so most of the CO_2 bubbles out of the solution. The decomposition reaction is

$$H_2CO_3(aq) \longrightarrow H_2O + CO_2(g)$$

Therefore, the overall molecular equation for the reaction is

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2O + CO_2(g)$$

The ionic equation is

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + HCO_3^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O + CO_2(g)$$

and the net ionic equation is

$$H^+(aq) + HCO_3^-(aq) \longrightarrow H_2O + CO_2(g)$$

Similar results are obtained if we begin with a carbonate instead of a bicarbonate. In this case, hydrogen ions combine with carbonate ions to give H_2CO_3, which subsequently decomposes to water and CO_2.

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2CO_3(aq) \longrightarrow H_2O + CO_2(g)$$

The net reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2O + CO_2(g)$$

Figure 5.23 | **Limestone reacts with acid.** Bubbles of CO_2 are formed in the reaction of limestone ($CaCO_3$) with hydrochloric acid. *(Andy Washnik)*

The release of CO_2 by the reaction of a carbonate with an acid is such a strong driving force for reaction that it enables insoluble carbonates to dissolve in acids (strong and weak). The reaction of limestone, $CaCO_3$, with hydrochloric acid is shown in Figure 5.23. The molecular and net ionic equations for the reaction are as follows:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O$$
$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

Carbon dioxide is not the only gas formed in metathesis reactions. Table 5.2 lists others and the reactions that form them.

Table 5.2 Gases Formed in Metathesis Reactions

Gases Formed in Reactions with Acids

Gas	Reactant Type	Equation for Formation[a]
H_2S	Sulfides	$2H^+ + S^{2-} \longrightarrow H_2S$
HCN	Cyanides	$H^+ + CN^- \longrightarrow HCN$
CO_2	Carbonates	$2H^+ + CO_3^{2-} \longrightarrow (H_2CO_3) \longrightarrow H_2O + CO_2$
	Bicarbonates (hydrogen carbonates)	$H^+ + HCO_3^- \longrightarrow (H_2CO_3) \longrightarrow H_2O + CO_2$
SO_2	Sulfites	$2H^+ + SO_3^{2-} \longrightarrow (H_2SO_3) \longrightarrow H_2O + SO_2$
	Bisulfites (hydrogen sulfites)	$H^+ + HSO_3^- \longrightarrow (H_2SO_3) \longrightarrow H_2O + SO_2$

Gases Formed in Reactions with Bases

Gas	Reactant Type	Equation for Formation
NH_3	Ammonium salts[b]	$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

[a] Formulas in parentheses are of unstable compounds that break down according to the continuation of the sequence.

[b] In writing a metathesis reaction, you may be tempted sometimes to write NH_4OH as a formula for "ammonium hydroxide." This compound does not exist. In water, it is nothing more than a solution of NH_3.

TOOLS

Gases formed in metathesis reactions

CHEMISTRY OUTSIDE THE CLASSROOM 5.2

Hard Water and Its Problems

Precipitation reactions occur around us all the time, and we hardly ever take notice until they cause a problem. One common problem is caused by **hard water**—ground water that contains the "hardness ions," Ca^{2+}, Mg^{2+}, Fe^{2+}, or Fe^{3+}, in concentrations high enough to form precipitates with ordinary soap. Soap normally consists of the sodium salts of organic acids derived from animal fats or oils (so-called *fatty acids*). An example is sodium stearate, $NaC_{18}H_{35}O_2$. The negative ion of the soap forms an insoluble "scum" with hardness ions, which reduces the effectiveness of the soap for removing dirt and grease.

Hardness ions can be removed from water in a number of ways. One way is to add hydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, often called washing soda, to the water. The carbonate ion forms insoluble precipitates with the hardness ions; an example is $CaCO_3$.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

Once precipitated, the hardness ions are not available to interfere with the soap.

In localities where the earth contains limestone, which is composed mainly of $CaCO_3$, a particularly bothersome type of hard water is often found. Rain and other natural waters contain dissolved CO_2, which the water picks up from the atmosphere. Carbon dioxide is the anhydride of carbonic acid, H_2CO_3, a weak diprotic acid. This causes the water to be slightly acidic, primarily from the first step in the ionization of the acid,

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

As the slightly acidic water seeps through the limestone, some of the insoluble $CaCO_3$ dissolves to give soluble calcium bicarbonate.

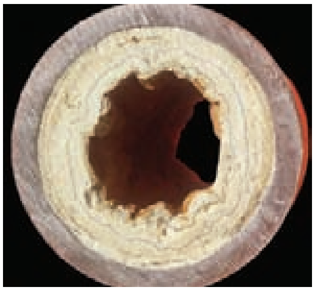
$$CaCO_3(s) + H_2CO_3(aq) \longrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

When this ground water is pumped and distributed in a community water supply, the presence of Ca^{2+} gives the kinds of problems discussed above.

A more serious problem occurs when this hard water is heated in hot water heaters or spattered onto glassware and the walls of shower stalls. When solutions containing Ca^{2+} and HCO_3^- are heated or when the water evaporates, the reverse reactions occur and insoluble $CaCO_3$ precipitates as follows.

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow H_2O + CO_2(g) + CaCO_3(s)$$

Evaporation of the hard water leaves spots of $CaCO_3$ on glass and other surfaces that are difficult to remove. In hot water heaters, the problem is more troublesome. The $CaCO_3$ precipitate sticks to the inner walls of pipes and the heating elements in hot water boilers and is called *boiler scale*. In locations that have high concentrations of Ca^{2+} and HCO_3^- in the water supply, boiler scale is a very serious problem, as illustrated in the photograph.



Boiler scale built up on the inside of a water pipe. *(Science VU/Betz/Visuals Unlimited.)*

Example 5.7
Predicting Reactions and Writing Their Equations

What reaction (if any) occurs when solutions of ammonium carbonate, $(NH_4)_2CO_3$, and propanoic acid (also called propionic acid), $HC_3H_5O_2$, are mixed?

■ **Analysis:** To determine whether a reaction occurs, we need to know whether a net ionic equation exists after we drop spectator ions from the ionic equation. We begin by writing a potential metathesis equation in molecular form. Then we examine the reactants and products to see whether any are weak electrolytes or substances that give gases. We also look for soluble or insoluble ionic compounds. Then we form the ionic equation and search for spectator ions, which we eliminate to obtain the net ionic equation.

■ **Assembling the Tools:** Our tools for working a problem such as this are the list of strong acids, the solubility rules (Table 5.1), and the list of gases formed in metathesis reactions (Table 5.2).

■ **Solution:** First we construct a molecular equation, treating the reaction as a metathesis. For the acid, we take the cation to be H^+ and the anion to be $C_3H_5O_2^-$. Therefore, after exchanging cations between the two anions we can obtain the following balanced molecular equation:

$$(NH_4)_2CO_3 + 2HC_3H_5O_2 \longrightarrow 2NH_4C_3H_5O_2 + H_2CO_3$$

In the statement of the problem we are told that we are working with a *solution* of $HC_3H_5O_2$, so we know it's soluble. Also, it is not on the list of strong acids (the first tool mentioned above), so we expect it to be a weak acid; we will write it in molecular form in the ionic equation.

Next, we recognize that H_2CO_3 decomposes into $CO_2(g)$ and H_2O. (This information is also found in Table 5.2.) Let's rewrite the molecular equation taking this into account.

$$(NH_4)_2CO_3 + 2HC_3H_5O_2 \longrightarrow 2NH_4C_3H_5O_2 + CO_2(g) + H_2O$$

Now we need to determine which of the ionic substances are soluble. According to the solubility rules, all ammonium salts are soluble, and we know that all salts are strong electrolytes. Therefore, we will write $(NH_4)_2CO_3$ and $NH_4C_3H_5O_2$ in dissociated form. Now we are ready to expand the molecular equation into the ionic equation.

$$2NH_4^+(aq) + CO_3^{2-}(aq) + 2HC_3H_5O_2(aq) \longrightarrow 2NH_4^+(aq) + 2C_3H_5O_2^-(aq) + CO_2(g) + H_2O$$

The only spectator ion is NH_4^+. Dropping this gives the net ionic equation.

$$CO_3^{2-}(aq) + 2HC_3H_5O_2(aq) \longrightarrow 2C_3H_5O_2^-(aq) + CO_2(g) + H_2O$$

A net reaction *does* occur, as indicated by the existence of a net ionic equation.

■ **Is the Answer Reasonable?** There are some common errors that people make in working problems of this kind, so it is important to double check. Be sure you've written the formulas of the products correctly. (If you need review, you might look at Example 5.6 on page 176.) Look for weak acids. (You need to know the list of strong ones; if an acid isn't on the list, it's a weak acid.) Look for gases, or substances that decompose into gases. (Be sure you've studied Table 5.2.) Check for insoluble compounds. (You need to know the solubility rules in Table 5.1.) If you've checked each step, it is likely your result is correct.

Example 5.8
Predicting Reactions and Writing Their Equations

What reaction (if any) occurs in water between potassium nitrate and ammonium chloride?

Analysis: Once again, we need to know whether a net ionic equation exists. We follow the same path as in Example 5.7, but first we have to convert the names of the compounds into chemical formulas. Then we construct molecular, ionic, and net ionic equations.

Assembling the Tools: The tools we need are (1) nomenclature rules from Chapter 3 and (2) the solubility rules (Table 5.1). No acids are mentioned among the reactants, so we don't need the list of strong acids. We're also not going to need Table 5.2. The products shown in that table are formed from the reaction of either an acid or a strong base, neither of which is among our reactants here.

Solution: First we apply the nomenclature rules. The ions in potassium nitrate are K^+ and NO_3^-, so the salt has the formula KNO_3. In ammonium chloride, the ions are NH_4^+ and Cl^-, so the salt is NH_4Cl.

Next we write the molecular equation, being sure to construct correct formulas for the products.

$$KNO_3 + NH_4Cl \longrightarrow KCl + NH_4NO_3$$

Looking over the substances in the equation, we don't find any that are weak acids or that decompose to give gases. Next, we check solubilities.

According to solubility Rule 2, both KNO_3 and NH_4Cl are soluble. By solubility Rules 1 and 2, both products are also soluble in water. The anticipated molecular equation is therefore

$$\underset{\text{soluble}}{KNO_3(aq)} + \underset{\text{soluble}}{NH_4Cl(aq)} \longrightarrow \underset{\text{soluble}}{KCl(aq)} + \underset{\text{soluble}}{NH_4NO_3(aq)}$$

and the ionic equation is

$$K^+(aq) + NO_3^-(aq) + NH_4^+(aq) + Cl^-(aq) \longrightarrow K^+(aq) + Cl^-(aq) + NH_4^+(aq) + NO_3^-(aq)$$

Notice that the right side of the equation is the same as the left side except for the order in which the ions are written. When we eliminate spectator ions, everything goes. There is no net ionic equation, which means there is no net reaction.

Is the Answer Reasonable? Once again, we perform the same checks here as in Example 5.7, and they tell us our answer is right.

Practice Exercises

5.24 | Knowing that salts of the formate ion, CHO_2^-, are water soluble, predict the reaction between $Co(OH)_2$ and formic acid, $HCHO_2$. Write molecular, ionic, and net ionic equations. (*Hint:* Apply the tools we used in Example 5.7.)

5.25 | Predict whether a reaction will occur in aqueous solution between the following pairs of substances: (a) $KCHO_2$ and HCl, (b) $CuCO_3$ and $HC_2H_3O_2$, (c) calcium acetate and silver nitrate, and (d) sodium hydroxide and nickel(II) chloride. Write molecular, ionic, and net ionic equations.

Using Metathesis Reactions to Synthesize Salts

One practical use for metathesis reactions is the synthesis of chemical compounds. For example, in the manufacture of photographic film, the light-sensitive component is a mixture of silver bromide and silver iodide formed by the reaction of silver nitrate with potassium bromide and iodide. Both reactants are water soluble, but the silver bromide and iodide are insoluble.

In planning a synthesis, the most important criterion is that the desired compound should be easily separated from the reaction mixture, uncontaminated by either the reactant starting materials or by any other product of the reaction. This leads to two principal approaches.

TOOLS

Synthesis by metathesis

1. If the desired compound is insoluble in water, then we can start with two soluble reactants. After the reaction is over, the compound can be separated from the mixture by filtration.
2. If the desired compound is soluble, the best route is either by an acid–base neutralization in which the anion is supplied by the acid and the cation by the base, or by a reaction in which the cation is from a metal carbonate and the anion is provided by an acid. (Metal sulfides or sulfites would work as well, but a product would then be H_2S or SO_2, both of which are poisonous gases.) In both cases, if the conditions are controlled correctly, the resulting solution can be evaporated to recover the desired product. These methods work best if one of the reactants is insoluble and is present in excess, so that the only soluble product remaining in the reaction mixture is the desired compound.

Example 5.9
Synthesizing a Compound by Metathesis

What reaction might we use to synthesize nickel sulfate, $NiSO_4$?

Analysis: Questions of this kind are somewhat open ended because there is often more than one reaction we can use to make the same compound. First we need to know whether $NiSO_4$ is soluble or not. Then we can select our reactants.

Assembling the Tools: One tool we are definitely going to need is the solubility rules. The better you know them, the easier answering the question will be. After deciding solubility, we use the decision-making tool above to determine our path. We may also need to know how to write equations for acid–base neutralization or reactions of acids with carbonates.

Solution: According to the solubility rules, $NiSO_4$ is soluble in water. This means our path is best followed by reaction of an acid with a base or a carbonate. The acid supplies the anion, so we would use H_2SO_4. The base would be $Ni(OH)_2$, and if we use a carbonate it would be $NiCO_3$. The solubility rules tell us both of these nickel-containing reactants are insoluble. Here are the two possible reactions written in molecular form.

$$H_2SO_4(aq) + Ni(OH)_2(s) \longrightarrow NiSO_4(aq) + 2H_2O$$

$$H_2SO_4(aq) + NiCO_3(s) \longrightarrow NiSO_4(aq) + CO_2(g) + H_2O$$

Is the Answer Reasonable? All we can do here is check the reasoning, which seems sound. The two equations yield the desired product, and if the reaction is carried out with an excess of the insoluble reactant, filtration will give a solution containing only $NiSO_4$.

Practice Exercises

5.26 | Write an equation for the preparation of copper(II) nitrate using an acid–base neutralization reaction.

5.27 | Suppose you wished to prepare cobalt(II) sulfide using a metathesis reaction. What criteria would the reactants have to satisfy *in this particular case*? Write an equation for a reaction utilizing a set of reactants that meet these criteria.

5.6 | Molarity

Solutions are very convenient for carrying out many reactions, and to deal with their stoichiometry we need to develop some quantitative tools. One of these is a way to express their *concentrations*. Earlier we used percentage concentration (grams of solute per 100 g of solution) as an example of a concentration unit. To deal with the stoichiometry of reactions in solution, however, percentage concentration is inconvenient. Instead, we express the amount of solute in moles and the amount of solution in liters.

The **molar concentration**, or **molarity** (abbreviated M), of a solution is defined as *the number of moles of solute per liter of solution*. It is a ratio of moles of solute to the volume of the solution expressed in liters.

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{5.4}$$

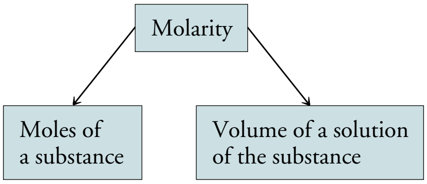
TOOLS Molarity

Thus, a solution that contains 0.100 mol of NaCl in 1.00 L has a molarity of 0.100 M, and we would refer to this solution as 0.100 *molar* NaCl or as 0.100 M NaCl. The same concentration would result if we dissolved 0.0100 mol of NaCl in 0.100 L (100 mL) of solution, because the *ratio* of moles of solute to volume of solution is the same.

$$\frac{0.100\text{ mol NaCl}}{1.00\text{ L NaCl soln}} = \frac{0.0100\text{ mol NaCl}}{0.100\text{ L NaCl soln}} = 0.100\ M\text{ NaCl}$$

Using Molarity as a Conversion Factor

Whenever we have to deal with a stoichiometry problem that involves an amount of a chemical and a volume of a solution of that substance, you can expect that solving the problem will involve molarity.



Molarity is a tool that provides the conversion factors we need to convert between moles and volume (either in liters or milliliters). Consider, for example, a solution labeled 0.100 M NaCl. The unit M always translates to mean "moles per liter," so we can write

$$0.100\,M\text{ NaCl} = \frac{0.100\text{ mol NaCl}}{1.00\text{ L soln}}$$

This gives us an equivalence relationship between "mol NaCl" and "L soln" that we can use to form two conversion factors[10].

$$\begin{tikzcd} & 0.100\text{ mol NaCl} \Leftrightarrow 1.00\text{ L soln} \arrow[dl] \arrow[dr] & \\ \dfrac{0.100\text{ mol NaCl}}{1.00\text{ L NaCl soln}} & & \dfrac{1.00\text{ L NaCl soln}}{0.100\text{ mol NaCl}} \end{tikzcd}$$

---

[10] Some students find it easier to translate the "1.00 L" part of these factors into the equivalent 1000 mL here rather than convert between liters and milliliters at some other stage of the calculation. Factors such as the two above, therefore, can be rewritten as follows whenever it is convenient. (Remember that "1000" in the following is regarded as having an infinite number of significant figures because, standing as it does for 1 L, it is part of the definition of molarity and is an exact number.)

$$\frac{0.100\text{ mol NaCl}}{1000\text{ mL NaCl soln}} \quad \text{and} \quad \frac{1000\text{ mL NaCl soln}}{0.100\text{ mol NaCl}}$$

Example 5.10

Calculating the Molarity of a Solution

To study the effect of dissolved salt on the rusting of an iron sample, a student prepared a solution of NaCl by dissolving 1.461 g of NaCl in enough water to make 250.0 mL of solution. What is the molarity of this solution?

■ **Analysis:** When given the amount of solute and the volume of a solution, we go back to the definition of molarity to calculate the concentration.

■ **Assembling the Tools:** The tool we'll use to solve this problem is Equation 5.4, which defines molarity as the ratio of *moles of solute* to *liters of solution.* If we can find these two pieces of information, we can arrange them as a ratio,

$$\text{molarity} = \frac{?\,\text{mol NaCl}}{?\,\text{L soln}}$$

■ If necessary, practice converting between liters and milliliters. It's a task you will have to perform frequently.

Therefore, we have to convert 1.461 g of NaCl to moles of NaCl, and the tool for this is the molar mass. We also have to change 250.0 mL to liters. The tool for this is 1000 mL = 1 L.

■ Once again, we carry one extra significant figure in intermediate calculations.

■ **Solution:** The number of moles of NaCl is found using the formula mass of NaCl, 58.443 g mol^{-1}.

$$1.461\ \cancel{\text{g NaCl}} \times \frac{1\ \text{mol}\ \cancel{\text{NaCl}}}{58.443\ \text{g NaCl}} = 0.024999\ \text{mol NaCl}$$

To find the volume of the solution in liters, we move the decimal three places to the left, so 250.0 mL equals 0.2500 L.

The ratio of moles to liters, therefore, is

$$\frac{0.024999\ \text{mol NaCl}}{0.2500\ \text{L}} = 0.1000\ M\ \text{NaCl}$$

■ **Is the Answer Reasonable?** Let's use our answer to do a rough calculation of the amount of NaCl in the solution. If our answer is right, we should find a value not too far from the amount given in the problem (1.461 g). If we round the formula mass of NaCl to 60, and use 0.1 M as an approximate concentration, then one liter of the solution contains 0.1 mol of NaCl, or approximately 6 g of NaCl (one-tenth of 60 g). But 250 mL is only 1/4 of a liter, so the mass of NaCl will be approximately 1/4 of 6 g, or about 1.5 g. This is pretty close to the amount that was given in the problem, so our answer is probably correct.

Practice Exercises

5.28 | A certain solution contains 16.9 g of HNO_3 dissolved in 125 mL of solution. Water is added until the volume is 175 mL. What is the molarity of HNO_3 in the final solution? (*Hint:* Does the amount of HNO_3 change when the water is added?)

5.29 | Suppose 1.223 g of NaCl is added to the 250.0 mL of NaCl solution described in Example 5.10. If there is no change in the total volume of the solution, what is the new molarity of the NaCl?

Example 5.11
Using Molar Concentrations

How many milliliters of 0.250 M NaCl solution must be measured to obtain 0.100 mol of NaCl?

■ **Analysis:** We can restate the problem as follows:

$$0.100 \text{ mol NaCl} \Leftrightarrow \text{? mL soln}$$

To find the answer, we need a conversion factor to take us from moles to milliliters. In the discussion above we say that moles and volume are related by the molarity.

■ **Assembling the Tools:** Our tool will be the molarity, which translates to

$$0.250\,M \text{ NaCl} = \frac{0.250 \text{ mol NaCl}}{1 \text{ L NaCl soln}}$$

The fraction on the right relates moles of NaCl to liters of the solution and provides us with two conversion factors.

$$\frac{0.250 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}} \quad \text{and} \quad \frac{1.00 \text{ L NaCl soln}}{0.250 \text{ mol NaCl}}$$

To obtain the answer, we select the one on the right, which will allow us to cancel the unit "mol NaCl."

■ **Solution:** We operate with the second factor on 0.100 mol NaCl.

$$0.100 \cancel{\text{mol NaCl}} \times \frac{1.00 \text{ L NaCl soln}}{0.250 \cancel{\text{mol NaCl}}} = 0.400 \text{ L of } 0.250\ M \text{ NaCl}$$

Because 0.400 L corresponds to 400 mL, our answer is that 400 mL (or 4.00×10^2 mL) of 0.250 M NaCl provides 0.100 mol of NaCl.

■ **Is the Answer Reasonable?** The molarity tells us that one liter contains 0.250 mol NaCl, so we need somewhat less than half of a liter (1000 mL) to obtain just 0.100 mol. The answer, 400 mL, is reasonable.

Practice Exercises

5.30 | A student measured 175 mL of 0.250 M HCl solution into a beaker. How many moles of HCl were in the beaker? (*Hint:* Molarity gives the equivalence between moles of solute and volume of solution in liters.)

5.31 | How many milliliters of 0.250 M HCl solution contain 1.30 g of HCl?

Obtaining Moles of Solute from Molarity and Volume

If you worked Practice Exercise 5.30 you learned that we can use the volume and molarity of a solution to calculate the number of moles of solute in it. This is such a useful relationship that it warrants special attention. Solving Equation 5.4 for *moles of solute* gives

TOOLS

Molarity times volume gives moles

$$\text{molarity} \times \text{volume (L)} = \text{moles of solute} \tag{5.5}$$

$$\frac{\text{mol solute}}{\cancel{\text{L soln}}} \times \cancel{\text{L soln}} = \text{mol solute}$$

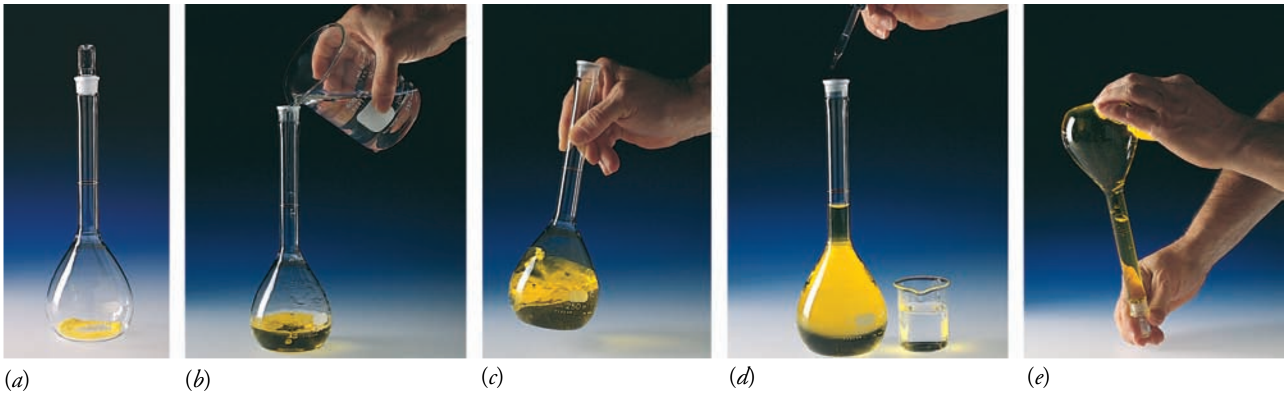


Figure 5.24 | **The preparation of a solution having a known molarity.** (*a*) The 250 mL volumetric flask shown is one of a number of sizes available for preparing solutions. When filled to the line etched around its neck, this flask contains exactly 250 mL of solution. The flask here already contains a weighed amount of solute. (*b*) Water is being added. (*c*) The solute is completely dissolved into solution before the level is brought up to the narrow neck of the flask. (*d*) More water is added to bring the level of the solution to the etched line. (*e*) The flask is stoppered and then inverted several times to mix its contents thoroughly. *(Michael Watson)*

Thus, *any time you know both the molarity and volume of a solution, you can easily calculate the number of moles of solute in it.* As you will see, this concept will be very useful in solving a variety of problems.

One situation in which Equation 5.5 is useful is when we must prepare some specific volume of a solution having a desired molarity (e.g., 250.0 mL of 0.0800 M Na_2CrO_4). To proceed, we have to calculate the amount of solute that will be in the solution after it's made. Thus, in 250.0 mL of 0.0800 M Na_2CrO_4 there are

- In this calculation, we're using molarity as a conversion factor to change volume to moles.

$$\frac{0.0800 \text{ mol Na}_2\text{CrO}_4}{1 \cancel{\text{L soln}}} \times 0.2500 \cancel{\text{L soln}} = 0.0200 \text{ mol Na}_2\text{CrO}_4$$

Figure 5.24 shows how we would use a 250-mL volumetric flask to prepare such a solution.[11] (A **volumetric flask** is a narrow-necked flask having an etched mark high on its neck. When filled to the mark, the flask contains precisely the volume given by the flask's label.)

Example 5.12
Preparing a Solution with a Known Molarity

Strontium nitrate, $Sr(NO_3)_2$, is used in fireworks to produce brilliant red colors. Suppose we need to prepare 250.0 mL of 0.100 M $Sr(NO_3)_2$ solution. How many grams of strontium nitrate are required?

Analysis: The *critical link* in solving this problem is realizing that we know both the volume and molarity of the final solution, which permits us to calculate the number of moles of $Sr(NO_3)_2$ that will be in it. Once we know the number of moles of $Sr(NO_3)_2$, we can calculate its mass using the molar mass of the salt.

Assembling the Tools: The first tool we will use is Equation 5.5.

$$\text{molarity of Sr(NO}_3)_2 \times \text{volume of solution in liters} = \text{moles Sr(NO}_3)_2$$

---

[11] Note that in preparing the solution described in Figure 5.24, we do not simply add 250 mL of water to the solute. If we did, the final volume would be slightly larger than 250 mL, which would make the molarity slightly less than desired. To obtain an accurate molarity, we add enough water to give a total volume of 250 mL. The actual volume of water added is not important, only that the *total final volume* is 250 mL.

Then we will use the molar mass of Sr, which gives us

$$1 \text{ mol } Sr(NO_3)_2 = 211.62 \text{ g } Sr(NO_3)_2$$

from which we will construct the necessary conversion factor.

Solution: First we apply Equation 5.5. The volume 250.0 mL converts to 0.2500 L. Multiplying the molarity by the volume in liters takes the following form.

$$\underset{\underset{\text{molarity}}{\uparrow}}{\frac{0.100 \text{ mol } Sr(NO_3)_2}{1.00 \cancel{\text{ L } Sr(NO_3)_2 \text{ soln}}}} \times \underset{\underset{\text{volume (L)}}{\uparrow}}{0.2500 \cancel{\text{ L } Sr(NO_3)_2 \text{ soln}}} = \underset{\underset{\text{moles of solute}}{\uparrow}}{0.02500 \text{ mol } Sr(NO_3)_2}$$

Finally, we convert from moles to grams using the molar mass of $Sr(NO_3)_2$.

$$0.02500 \cancel{\text{ mol } Sr(NO_3)_2} \times \frac{211.62 \text{ g } Sr(NO_3)_2}{1 \cancel{\text{ mol } Sr(NO_3)_2}} = 5.29 \text{ g } Sr(NO_3)_2$$

Thus, to prepare the solution we need to dissolve 5.29 g of $Sr(NO_3)_2$ in a total volume of 250.0 mL.

We could also have set this up as a chain calculation as follows, with the conversion factors strung together.

$$0.2500 \cancel{\text{ L } Sr(NO_3)_2 \text{ soln}} \times \frac{0.100 \cancel{\text{ mol } Sr(NO_3)_2}}{1.00 \cancel{\text{ L } Sr(NO_3)_2 \text{ soln}}} \times \frac{211.62 \text{ g } Sr(NO_3)_2}{1 \cancel{\text{ mol } Sr(NO_3)_2}} = 5.29 \text{ g } Sr(NO_3)_2$$

Is the Answer Reasonable? If we were working with a full liter of this solution, it would contain 0.1 mol of $Sr(NO_3)_2$. The molar mass of the salt is 211.62 g mol^{-1}, so 0.1 mol is slightly more than 20 g. However, we are working with just a quarter of a liter (250 mL), so the amount of $Sr(NO_3)_2$ needed is slightly more than a quarter of 20 g, or 5 g. The answer, 5.29 g, is close to this, so it makes sense.

Practice Exercises

5.32 | Suppose you wanted to prepare 50 mL of 0.2 M $Sr(NO_3)_2$ solution. Using the kind of approximate arithmetic we employed in the ***Is the Answer Reasonable*** step in Example 5.12, estimate the number of grams of $Sr(NO_3)_2$ required. (*Hint:* How many moles of $Sr(NO_3)_2$ would be in one liter of the solution?)

5.33 | How many grams of $AgNO_3$ are needed to prepare 250.0 mL of 0.0125 M $AgNO_3$ solution?

Diluting Solutions

Laboratory chemicals are usually purchased in concentrated form and must be *diluted* (made less concentrated) before being used. This is accomplished by adding more solvent to the solution, which spreads the solute through a larger volume and causes the concentration (the amount per unit volume) to decrease.

During dilution, the number of moles of solute remains constant. This means that the product of molarity and volume, which equals the moles of solute, must be the same for both the concentrated and diluted solution.

$$\underbrace{\begin{pmatrix}\text{Volume of}\\ \text{dilute solution}\\ \textit{to be prepared}\end{pmatrix} \times M_{\text{dilute}}}_{\substack{\text{Moles of solute in}\\ \text{the dilute solution}}} = \underbrace{\begin{pmatrix}\text{Volume of}\\ \text{concentrated solution}\\ \textit{to be used}\end{pmatrix} \times M_{\text{conc}}}_{\substack{\text{Moles of solute in the}\\ \text{concentrated solution}}}$$

Or,

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}} \qquad (5.6)$$

TOOLS

Dilution equation

Any units can be used for volume in Equation 5.6 provided that they are the same on both sides of the equation. This means we can solve dilution problems using *milliliters* directly in Equation 5.6.

Example 5.13
Preparing a Solution of Known Molarity by Dilution

How can we prepare 100.0 mL of 0.0400 M $K_2Cr_2O_7$ from 0.200 M $K_2Cr_2O_7$?

Analysis: This is the way such a question comes up in the lab, but what it is really asking is, "How many milliliters of 0.200 M $K_2Cr_2O_7$ (the more concentrated solution) must be diluted to give a solution with a final volume of 100.0 mL and a final molarity of 0.0400 M?" Once we see the question this way, it becomes clear what we have to do.

Assembling the Tools: Because it's a dilution problem, the tool we need to solve the problem is Equation 5.6.

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}}$$

Solution: It's a good idea to assemble the data first, noting what is missing (and therefore what has to be calculated).

$$V_{\text{dil}} = 100.0 \text{ mL} \qquad M_{\text{dil}} = 0.0400\ M$$

$$V_{\text{conc}} = ? \qquad M_{\text{conc}} = 0.200\ M$$

Next, we substitute into Equation 5.6.

$$100.0 \text{ mL} \times 0.0400\ M = V_{\text{conc}} \times 0.200\ M$$

Solving for V_{conc} gives

$$V_{\text{conc}} = \frac{100.0 \text{ mL} \times 0.0400\ M}{0.200\ M}$$
$$= 20.0 \text{ mL}$$

Therefore, the answer to the question as asked is: We would withdraw 20.0 mL of 0.200 M $K_2Cr_2O_7$, place it in a 100 mL volumetric flask, and then add water until the final volume is exactly 100 mL. (See Figure 5.25.)

Is the Answer Reasonable? Notice that the concentrated solution is 5 times more concentrated than the dilute solution ($5 \times 0.04 = 0.2$). To reduce the concentration by a factor of 5 requires that we increase the volume by a factor of 5, and we see that 100 mL is 5 times 20 mL. The answer appears to be correct.

Practice Exercises

5.34 | To what final volume must 100.0 mL of 0.125 M H_2SO_4 solution be diluted to give a 0.0500 M H_2SO_4 solution? (*Hint:* Write the equation we used for dilution problems.)

5.35 | How many milliliters of water have to be *added* to 150 mL of 0.50 M HCl to reduce the concentration to 0.10 M HCl?

5.7 | Solution Stoichiometry

When we deal quantitatively with reactions in solution, we often work with volumes of solutions and molarity. The following is an example.

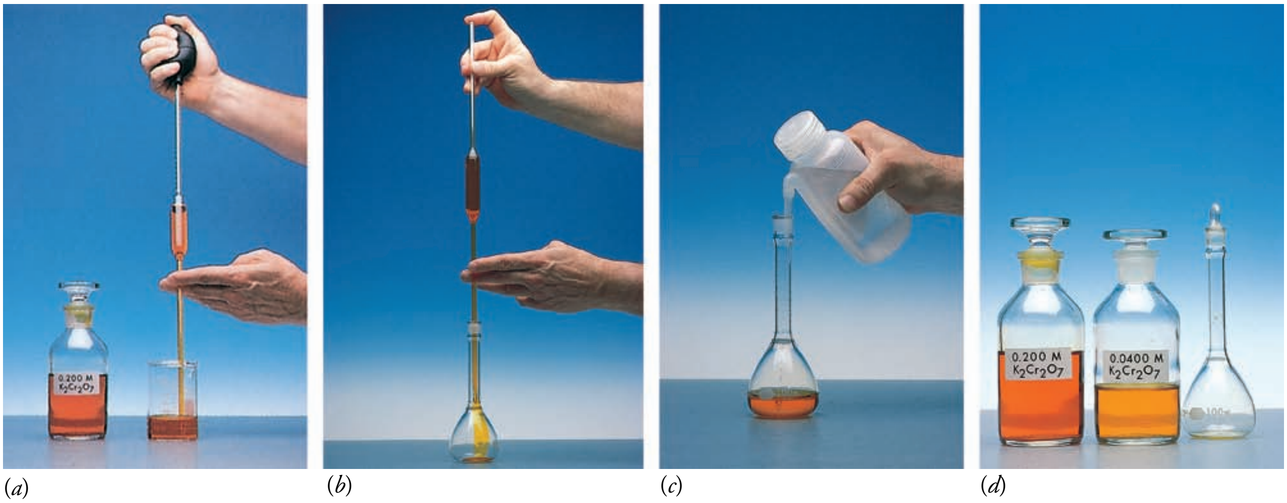


Figure 5.25 | **Preparing a solution by dilution.** (*a*) The calculated volume of the more concentrated solution is withdrawn from the stock solution by means of a volumetric pipet. (*b*) The solution is allowed to drain entirely from the pipet into the volumetric flask. (*c*) Water is added to the flask, the contents are mixed, and the final volume is brought up to the etch mark on the narrow neck of the flask. (*d*) The new solution is put into a labeled container. *(OPC, Inc.)*

Example 5.14

Stoichiometry Involving Reactions in Solution

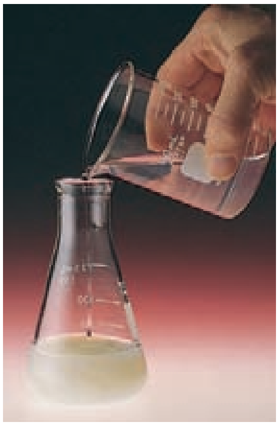
One of the solids present in photographic film is silver bromide, AgBr. Suppose we wanted to prepare AgBr by the following precipitation reaction.

$$2AgNO_3(aq) + CaBr_2(aq) \longrightarrow 2AgBr(s) + Ca(NO_3)_2(aq)$$

How many milliliters of 0.125 *M* $CaBr_2$ solution must be used to react with the solute in 50.0 mL of 0.115 *M* $AgNO_3$?

Analysis: In general, when we deal with the stoichiometry of a reaction, we work with a balanced chemical equation, which we're given. The coefficients in the equation will relate moles of $CaBr_2$ to moles of $AgNO_3$, so this will be one of the tools we will use. However, we're not given moles directly. Instead we have molarities and the volume of the $AgNO_3$ solution. The *critical link* in solving the problem is recognizing that the molarity and volume of the $AgNO_3$ solution provides a path to finding the number of moles of $AgNO_3$.

At this point we can go in two steps from the data given for the $AgNO_3$ solution to the number of moles of $CaBr_2$ that react. The last step will be to go from moles of $CaBr_2$ to milliliters of the solution, and these two quantities are related by the molarity of the $CaBr_2$ solution. The calculation flow will look like the following.



Silver bromide (AgBr) precipitates when solutions of calcium bromide and silver nitrate are mixed. *(Michael Watson)*

$$\begin{tikzcd}
 & \text{mol } AgNO_3 \arrow[r, "\text{coefficients of}", "\text{balanced equation}"'] & \text{mol } CaBr_2 \arrow[dr, "\text{moles of } CaBr_2 \text{ and molarity of } CaBr_2 \text{ solution}"] & \\
\mathbf{AgNO_3}\ \textbf{soln} \arrow[ur, "\text{volume and molarity of } AgNO_3 \text{ solution}"] & & & \mathbf{CaBr_2}\ \textbf{soln}
\end{tikzcd}$$

Given: 50.0 mL of 0.115 *M* $AgNO_3$

To find: ? mL of 0.125 *M* $CaBr_2$

Assembling the Tools: Here are the tools we will use. First, we need the relationship to calculate moles of $AgNO_3$

$$\text{molarity } AgNO_3 \text{ soln} \times \text{volume } AgNO_3 \text{ soln(L)} = \text{moles } AgNO_3$$

The next tool uses the coefficients of the equation.

$$2\text{ mol AgNO}_3 \Leftrightarrow 1\text{ mol CaBr}_2$$

Finally, we go from moles of $CaBr_2$ to volume of solution using the relationship derived from the molarity (0.125 M $CaBr_2$),

$$0.125\text{ mol CaBr}_2 \Leftrightarrow 1.00\text{ L CaBr}_2\text{ soln}$$

to form the necessary conversion factor.

Solution: First, we find the moles of $AgNO_3$ taken. Changing 50.0 mL to 0.0500 L,

$$0.0500\ \overset{\text{volume}}{\cancel{\text{L AgNO}_3\text{ soln}}} \times \overset{\text{molarity}}{\frac{0.115\text{ mol AgNO}_3}{1.00\ \cancel{\text{L AgNO}_3\text{ soln}}}} = 5.75\times10^{-3}\text{ mol AgNO}_3$$

Next, we use the coefficients of the equation to calculate the amount of $CaBr_2$ required.

$$5.75\times10^{-3}\ \cancel{\text{mol AgNO}_3} \times \frac{1\text{ mol CaBr}_2}{2\ \cancel{\text{mol AgNO}_3}} = 2.875\times10^{-3}\text{ mol CaBr}_2$$

Finally we calculate the volume (mL) of 0.125 M $CaBr_2$ that contains this many moles of $CaBr_2$. Here we use the fact that the molarity of the $CaBr_2$ solution, 0.125 M, gives two possible conversion factors:

$$\frac{0.125\text{ mol CaBr}_2}{1.00\text{ L CaBr}_2\text{ soln}} \quad \text{and} \quad \frac{1.00\text{ L CaBr}_2\text{ soln}}{0.125\text{ mol CaBr}_2}$$

We use the one that cancels the unit "mol $CaBr_2$."

$$2.875\times10^{-3}\ \cancel{\text{mol CaBr}_2} \times \frac{1.00\text{ L CaBr}_2\text{ soln}}{0.125\ \cancel{\text{mol CaBr}_2}} = 0.0230\text{ L CaBr}_2\text{ soln}$$

Thus 0.0230 L, or 23.0 mL, of 0.125 M $CaBr_2$ has enough solute to combine with the $AgNO_3$ in 50.0 mL of 0.115 M $AgNO_3$.

Is the Answer Reasonable? The molarities of the two solutions are about the same, but only 1 mol $CaBr_2$ is needed for each 2 mol $AgNO_3$. Therefore, the volume of $CaBr_2$ solution needed (23.0 mL) should be about half the volume of $AgNO_3$ solution taken (50.0 mL), which it is.

Practice Exercises

5.36 | How many milliliters of 0.0475 M H_3PO_4 could be completely neutralized by 45.0 mL of 0.100 M KOH? The balanced equation for the reaction is

$$H_3PO_4(aq) + 3KOH(aq) \longrightarrow K_3PO_4(aq) + 3H_2O$$

(*Hint:* Outline the path of the calculations as in Example 5.14.)

5.37 | How many milliliters of 0.124 M NaOH contain enough NaOH to react with the H_2SO_4 in 15.4 mL of 0.108 M H_2SO_4 according to the following equation?

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O$$

Using Net Ionic Equations in Calculations

In the preceding problem, we worked with a molecular equation in solving a stoichiometry problem. Ionic and net ionic equations can also be used, but this requires that we work with the concentrations of the ions in solution.

Calculating Concentrations of Ions in Solutions of Electrolytes

The concentrations of the ions in a solution of a strong electrolyte are obtained from the formula and molar concentration of the solute. For example, suppose we are working with a solution labeled "0.20 M $CaCl_2$." In 1.0 L of this solution there is 0.20 mol of $CaCl_2$, which is fully dissociated into Ca^{2+} and Cl^- ions.

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

Based on the stoichiometry of the dissociation, 1 mol Ca^{2+} and 2 mol Cl^- are formed from each 1 mol of $CaCl_2$. We can find the ion concentrations in the solution using dimensional analysis.

$$\frac{0.20 \cancel{\text{mol CaCl}_2}}{1.0 \text{ L soln}} \times \frac{1 \text{ mol Ca}^{2+}}{1 \cancel{\text{mol CaCl}_2}} = \frac{0.20 \text{ mol Ca}^{2+}}{1.0 \text{ L soln}} = 0.20\,M\,\text{Ca}^{2+}$$

$$\frac{0.20 \cancel{\text{mol CaCl}_2}}{1.0 \text{ L soln}} \times \frac{2 \text{ mol Cl}^-}{1 \cancel{\text{mol CaCl}_2}} = \frac{0.40 \text{ mol Cl}^-}{1.0 \text{ L soln}} = 0.40\,M\,\text{Cl}^-$$

In 0.20 M $CaCl_2$, then, the concentration of Ca^{2+} is 0.20 M and the concentration of Cl^- is 0.40 M.

■ If you should ever become confused, you can always fall back on dimensional analysis to check the calculation.

In the example just given, notice that the ion concentrations are equal to the concentration of $CaCl_2$ multiplied by the number of ions of each kind that are released when a formula unit of $CaCl_2$ dissociates. This provides a very simple way to find the concentrations of the ions.

> The concentration of a particular ion equals the concentration of the salt multiplied by the number of ions of that kind in one formula unit of the salt.

TOOLS

Molarity of ions in a salt solution

Example 5.15

Calculating the Concentrations of Ions in a Solution

What are the molar concentrations of the ions in 0.20 M aluminum sulfate?

■ **Analysis:** To find the molar concentrations, we first need the formulas of the ions so we can write the correct formula of aluminum sulfate. Then we will have to examine how the salt dissociates and use that information to calculate ion concentrations.

■ **Assembling the Tools:** Several tools are required: (1) the formulas of the ions and the rules for writing chemical formulas, both from Chapter 3, (2) the equation for the dissociation of the salt in water, and (3) the method we just developed for finding molar concentrations of the ions using the coefficients in the dissociation equation.

■ **Solution:** The ions are Al^{3+} and $SO_4{}^{2-}$, so the salt must be $Al_2(SO_4)_3$. When $Al_2(SO_4)_3$ dissolves, it dissociates as follows:

$$Al_2(SO_4)_3(s) \longrightarrow 2Al^{3+}(aq) + 3SO_4{}^{2-}(aq)$$

Each formula unit of $Al_2(SO_4)_3$ yields two Al^{3+} ions and three $SO_4{}^{2-}$ ions. Therefore, 0.20 mol $Al_2(SO_4)_3$ yields 0.40 mol Al^{3+} and 0.60 mol $SO_4{}^{2-}$, and we conclude that the solution contains 0.40 M Al^{3+} and 0.60 M $SO_4{}^{2-}$.

■ **Is the Answer Reasonable?** The answers here have been obtained by simple mole reasoning. We could have found the answers in a more formal manner using dimensional analysis. For example, for Al^{3+}, we have

$$\frac{0.20 \cancel{\text{mol Al}_2(\text{SO}_4)_3}}{1.0 \text{ L soln}} \times \frac{2 \text{ mol Al}^{3+}}{1 \cancel{\text{mol Al}_2(\text{SO}_4)_3}} = \frac{0.40 \text{ mol Al}^{3+}}{1.0 \text{ L soln}} = 0.40\,M\,\text{Al}^{3+}$$

A similar calculation would give the concentration of $SO_4{}^{2-}$ as 0.60 M. Study both methods. With just a little practice, you will have little difficulty with the reasoning approach we used first.

Example 5.16

Calculating the Concentration of a Salt from the Concentration of One of Its Ions

A student found that the sulfate ion concentration in a solution of $Al_2(SO_4)_3$ was 0.90 M. What was the concentration of $Al_2(SO_4)_3$ in the solution?

Analysis: Once again, we use the formula of the salt to determine the number of ions released when it dissociates. This time we use the information to work backward to find the salt concentration.

Assembling the Tools: The tools are the same as in Example 5.15.

Solution: Let's set up the problem using dimensional analysis to be sure of our procedure. We will use the fact that 1 mol $Al_2(SO_4)_3$ yields 3 mol SO_4^{2-} in solution.

$$1\ \text{mol Al}_2(\text{SO}_4)_3 \Leftrightarrow 3\ \text{mol SO}_4^{2-}$$

therefore,

$$\frac{0.90\ \cancel{\text{mol SO}_4^{2-}}}{1.0\ \text{L soln}} \times \frac{1\ \text{mol Al}_2(\text{SO}_4)_3}{3\ \cancel{\text{mol SO}_4^{2-}}} = \frac{0.30\ \text{mol Al}_2(\text{SO}_4)_3}{1.0\ \text{L soln}} = 0.30\ M\ \text{Al}_2(\text{SO}_4)_3$$

The concentration of $Al_2(SO_4)_3$ is 0.30 M.

Is the Answer Reasonable? We'll use the reasoning approach to check our answer. We know that 1 mol $Al_2(SO_4)_3$ yields 3 mol SO_4^{2-} in solution. Therefore, the number of moles of $Al_2(SO_4)_3$ is only one-third the number of moles of SO_4^{2-}. So the concentration of $Al_2(SO_4)_3$ must be one-third of 0.90 M, or 0.30 M.

Practice Exercises

5.38 | What are the molar concentrations of the ions in 0.40 M $FeCl_3$? (*Hint:* How many ions of each kind are formed when $FeCl_3$ dissociates?)

5.39 | In a solution of Na_3PO_4, the PO_4^{3-} concentration was determined to be 0.250 M. What was the sodium ion concentration in the solution?

Stoichiometry Calculations

You have seen that a net ionic equation is convenient for describing the net chemical change in an ionic reaction. Example 5.17 illustrates how such equations can be used in stoichiometric calculations.

Example 5.17

Stoichiometric Calculations Using a Net Ionic Equation

How many milliliters of 0.100 M $AgNO_3$ solution are needed to react completely with 25.0 mL of 0.400 M $CaCl_2$ solution? The net ionic equation for the reaction is

$$\text{Ag}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{AgCl}(s)$$

Analysis: In many ways, this problem is similar to Example 5.14. However, to use the net ionic equation, we will need to work with the concentrations of the ions. Therefore, to solve the problem, the first step will be to calculate the molarities of the ions in the solutions being mixed. Next, using the volume and molarity of the Cl^- solution, we will calculate the moles of Cl^- available. Then we'll use the coefficients of the equation to find the moles of Ag^+ that react. Finally, we'll use the molarity of the Ag^+ solution to determine the volume of the 0.100 M $AgNO_3$ solution needed.

Assembling the Tools: To obtain the concentrations of the ions in the solutions of reactants, the tool will be chemical formulas themselves: one $AgNO_3$ yields one Ag^+ and one NO_3^-; one $CaCl_2$ yields one Ca^{2+} and two Cl^-.

The second tool will be Equation 5.5,

$$\text{volume Cl}^-\ \text{soln} \times \text{molarity of Cl}^-\ \text{soln} = \text{moles Cl}^-$$

The next tool is provided by the coefficients in the equation:

$$1\ \text{mol Ag}^+ \Leftrightarrow 1\ \text{mol Cl}^-$$

The molarity of the Ag^+ solution gives us the relationship required to convert from moles of Ag^+ to the volume of solution.

Solution: We begin by applying the first tool and finding the concentrations of the ions in the reacting solutions.

$$\begin{array}{llll} 0.100\ M\ \text{AgNO}_3 & \text{contains } 0.100\ M\ \text{Ag}^+ & \text{and} & 0.100\ M\ \text{NO}_3^- \\ 0.400\ M\ \text{CaCl}_2 & \text{contains } 0.400\ M\ \text{Ca}^{2+} & \text{and} & 0.800\ M\ \text{Cl}^- \end{array}$$

We're only interested in the Ag^+ and Cl^-; the Ca^{2+} and NO_3^- are spectator ions. For our purposes, then, the solution concentrations are $0.100\ M\ Ag^+$ and $0.800\ M\ Cl^-$. Having these values, we can now restate the problem: How many milliliters of $0.100\ M\ Ag^+$ solution are needed to react completely with 25.0 mL of $0.800\ M\ Cl^-$ solution?

$$25.0\ \text{mL Cl}^-\ \text{soln} \Leftrightarrow ?\ \text{mL Ag}^+\ \text{soln}$$

The moles of Cl^- available for reaction are obtained from the molarity and volume (0.0250 L) of the Cl^- solution by applying our second tool.

$$0.0250\ \cancel{\text{L Cl}^-}\ \text{soln} \times \frac{0.800\ \text{mol Cl}^-}{1.00\ \cancel{\text{L Cl}^-}\ \text{soln}} = 0.0200\ \text{mol Cl}^-$$

$$\text{volume} \qquad \times \qquad \text{molarity} \qquad = \text{moles of solute}$$

The coefficients of the equation tell us the Ag^+ and Cl^- combine in a 1-to-1 mole ratio, so $0.0200\ \text{mol Cl}^- \Longleftrightarrow 0.0200\ \text{mol Ag}^+$. Finally, we calculate the volume of the Ag^+ solution using its molarity as a conversion factor. As we've done previously, we use the factor that makes the units cancel correctly.

Simple reasoning works well here. Since the coefficients of Ag^+ and Cl^- are the same, the numbers of moles that react must be equal.

$$0.0200\ \cancel{\text{mol Ag}^+} \times \frac{1.00\ \text{L Ag}^+\ \text{soln}}{0.100\ \cancel{\text{mol Ag}^+}} = 0.200\ \text{L Ag}^+\ \text{soln}$$

Our calculations tell us that we must use 0.200 L or 200 mL of the $AgNO_3$ solution. We could also have used the following chain calculation.

$$0.0250\ \cancel{\text{L Cl}^-}\ \text{soln} \times \frac{0.800\ \cancel{\text{mol Cl}^-}}{1.00\ \cancel{\text{L Cl}^-}\ \text{soln}} \times \frac{1\ \cancel{\text{mol Ag}^+}}{1\ \cancel{\text{mol Cl}^-}} \times \frac{1.00\ \text{L Ag}^+\ \text{soln}}{0.100\ \cancel{\text{mol Ag}^+}} = 0.200\ \text{L Ag}^+\ \text{soln}$$

Is the Answer Reasonable? The silver ion concentration is one-eighth as large as the chloride ion concentration. Since the ions react one-for-one, we will need eight times as much silver ion solution as chloride solution. Eight times the amount of chloride solution, 25 mL, is 200 mL, which is the answer we obtained. Therefore, the answer appears to be correct.

A solution of $AgNO_3$ is added to a solution of $CaCl_2$, producing a precipitate of AgCl. *(Andy Washnik)*

Practice Exercises

5.40 | Suppose 18.4 mL of $0.100\ M\ AgNO_3$ solution was needed to react completely with 20.5 mL of $CaCl_2$ solution. What is the molarity of the $CaCl_2$ solution? Use the net ionic equation in Example 5.17 to work the problem. (*Hint:* How can you calculate molarity from moles and volume, and how can you calculate the molarity of the $CaCl_2$ solution from the molarity of Cl^-?)

5.41 | How many milliliters of $0.500\ M$ KOH are needed to react completely with 60.0 mL of $0.250\ M\ FeCl_2$ solution to precipitate $Fe(OH)_2$? The net ionic equation is: $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$.

5.8 | Titrations and Chemical Analysis

Chemical analyses fall into two categories. In a **qualitative analysis** we simply determine which substances are present in a sample without measuring their amounts. In a **quantitative analysis**, our goal is to measure the amounts of the various substances in a sample.

When chemical reactions are used in a quantitative analysis, a useful strategy is to capture *all* of a desired chemical species in a compound with a known formula. From the amount of this compound obtained, we can determine how much of the desired chemical species was present in the original sample. Such an analysis was described in Example 4.12 on page 125 in which we described the combustion analysis of a compound of carbon, hydrogen, and oxygen. The following example illustrates a similar analysis using solution chemistry.

Example 5.18

Calculation Involving a Quantitative Analysis

A chemist was asked to analyze a solution of chlordane, $C_{10}H_6Cl_8$, dissolved in a hydrocarbon solvent that was discovered by construction workers during demolition of an old work shed. This insecticide was banned for sale in the United States in 1988 by the EPA because of its potential for causing cancer. Reactions were carried out on a 1.446 g sample of the solution which converted all of the chlorine to chloride ion dissolved in water. This aqueous solution required 91.22 mL of 0.1400 M $AgNO_3$ to precipitate all of the chloride ion as AgCl. What was the percentage of chlordane in the original solution? The precipitation reaction was

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Analysis: The percentage of chlordane in the sample will be calculated as follows:

$$\%\ C_{10}H_6Cl_8 \text{ by mass} = \frac{\text{mass of } C_{10}H_6Cl_8 \text{ in sample}}{\text{mass of sample}} \times 100\%$$

We already have the mass of the sample, so we need to use the data to calculate the mass of $C_{10}H_6Cl_8$. In doing this, we will assume that all the chlorine that was ultimately precipitated as AgCl originated in the chlordane and that none was lost in the reactions that had converted it to chloride ion.

From the molarity and volume of the $AgNO_3$ solution, we can calculate the moles of Ag^+ that reacts with Cl^-. The net ionic equation tells us Ag^+ and Cl^- react in a 1-to-1 mole ratio, so the moles of Ag^+ equals the moles of Cl^- that react. This equals the number of moles of Cl in the chlordane present in the sample of the solution. We will use the moles of Cl to calculate the moles of $C_{10}H_6Cl_8$ and then the grams of $C_{10}H_6Cl_8$. Once we have the mass of $C_{10}H_6Cl_8$ we can calculate the percentage of $C_{10}H_6Cl_8$.

Assembling the Tools: Equation 5.5 is the tool with which we calculate moles of Ag^+ that react.

$$\text{molarity of } Ag^+ \text{ soln} \times \text{volume of } Ag^+ \text{ soln} = \text{moles of } Ag^+$$

As noted, the net ionic equation tells us that moles of Ag^+ equals moles of Cl^-, which equals moles Cl.

The formula for chlordane gives us the equivalence

$$1 \text{ mol } C_{10}H_6Cl_8 \Leftrightarrow 8 \text{ mol Cl}$$

which allows us to calculate the moles of $C_{10}H_6Cl_8$ in the sample from the moles of Cl. To find grams of $C_{10}H_6Cl_8$, we need the molar mass of $C_{10}H_6Cl_8$, which is 409.778 g mol^{-1}.

$$1 \text{ mol } C_{10}H_6Cl_8 \Leftrightarrow 409.778 \text{ g}$$

■ **Solution:** In 0.1400 *M* $AgNO_3$, the molarity of Ag^+ is 0.1400 *M*. Applying Equation 5.5,

$$0.09122\ \text{L}\ \cancel{\text{Ag}^+\ \text{soln}} \times \frac{0.1400\ \text{mol Ag}^+}{1.000\ \cancel{\text{L Ag}^+\ \text{soln}}} = 0.012771\ \text{mol Ag}^+$$

■ 91.22 mL = 0.09122 L.

From the stoichiometry of the equation,

$$0.012771\ \text{mol Ag}^+ \Leftrightarrow 0.012771\ \text{mol Cl}^-$$

This is the amount of Cl^- that came from the sample, so the chlordane in the sample must have contained 0.012771 mol Cl. Now we use the formula for chlordane to calculate moles of $C_{10}H_6Cl_8$ in the sample.

$$0.012771\ \cancel{\text{mol Cl}} \times \frac{1\ \text{mol C}_{10}\text{H}_6\text{Cl}_8}{8\ \cancel{\text{mol Cl}}} = 1.5964 \times 10^{-3}\ \text{mol C}_{10}\text{H}_6\text{Cl}_8$$

Using the formula mass of chlordane, we calculate the mass of the insecticide in the sample.

$$1.5964 \times 10^{-3}\ \cancel{\text{mol C}_{10}\text{H}_6\text{Cl}_8} \times \frac{409.778\ \text{g C}_{10}\text{H}_6\text{Cl}_8}{1\ \cancel{\text{mol C}_{10}\text{H}_6\text{Cl}_8}} = 0.65417\ \text{g C}_{10}\text{H}_6\text{Cl}_8$$

The percentage of chlordane in the sample was

$$\%\ \text{C}_{10}\text{H}_6\text{Cl}_8 = \frac{0.65417\ \text{g C}_{10}\text{H}_6\text{Cl}_8}{1.446\ \text{g sample}} \times 100\% = 45.24\% \quad \text{(rounded correctly)}$$

The solution of insecticide contained 45.24% chlordane by mass.

■ **Is the Answer Reasonable?** We have used approximately 0.1 L of 0.14 *M* Ag^+ solution, which contains 0.014 mol of Ag^+. The amount of Cl^- consumed is also 0.014 mol, which is the amount of Cl in the chlordane. The moles of chlordane are 1/8th of 0.014. For simplicity, suppose it was 1/10th. The moles of chlordane would then be 0.0014 mol. With a molar mass of about 400 g mol^{-1}, 0.001 mol of $C_{10}H_6Cl_8$ would weigh 0.4 g and 0.0014 mol would weigh around 0.6 g. Our answer, 0.654 g, is not far from this, so the calculations seem to be correct.

Practice Exercises

5.42 | A solution containing Na_2SO_4 was treated with 0.150 *M* $BaCl_2$ solution until all the sulfate ion had reacted to form $BaSO_4$. The net reaction

$$\text{Ba}^{2+}(aq) + \text{SO}_4^{\ 2-}(aq) \longrightarrow \text{BaSO}_4(s)$$

required 28.40 mL of the $BaCl_2$ solution. How many grams of Na_2SO_4 were in the solution? (*Hint:* How do moles of $SO_4^{\ 2-}$ relate to moles of Na_2SO_4?)

5.43 | A sample of a mixture containing $CaCl_2$ and $MgCl_2$ weighed 2.000 g. The sample was dissolved in water, and H_2SO_4 was added until the precipitation of $CaSO_4$ was complete.

$$\text{CaCl}_2(aq) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{CaSO}_4(s) + 2\text{HCl}(aq)$$

The $CaSO_4$ was filtered, dried completely, and weighed. A total of 0.736 g of $CaSO_4$ was obtained.

(a) How many moles of Ca^{2+} were in the $CaSO_4$?
(b) How many moles of Ca^{2+} were in the original 2.000 g sample?
(c) How many moles of $CaCl_2$ were in the 2.000 g sample?
(d) How many grams of $CaCl_2$ were in the 2.000 g sample?
(e) What was the percentage by mass of $CaCl_2$ in the original mixture?
(f) What was the percentage by mass of $MgCl_2$ in the original mixture?

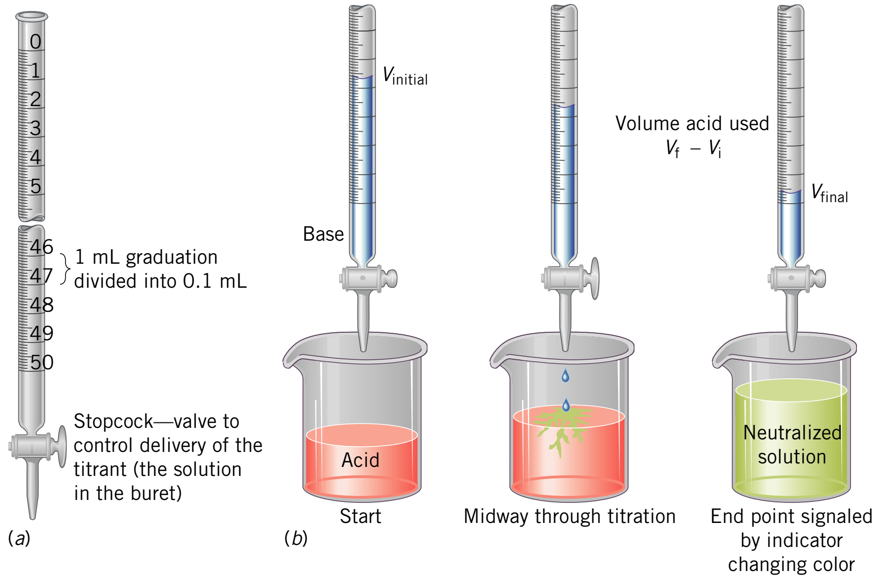

0
1
2
3
4
5
46
47
48
49
50
1 mL graduation divided into 0.1 mL
Stopcock—valve to control delivery of the titrant (the solution in the buret)
(a)
(b)
V_{initial}
Base
Acid
Start
Midway through titration
Volume acid used
$V_f - V_i$
V_{final}
Neutralized solution
End point signaled by indicator changing color

Figure 5.26 | **Titration.** (*a*) A buret. (*b*) The titration of an acid by a base in which an acid-base indicator is used to signal the end point, which is the point at which all of the acid has been neutralized and addition of the base is halted.

Acid–Base Titrations

Titration is an important laboratory procedure used in performing chemical analyses. The apparatus is shown in Figure 5.26. The long tube is called a **buret**, which is marked for volumes, usually in increments of 0.10 mL. The valve at the bottom of the buret is called a **stopcock**, and it permits the analyst to control the amount of **titrant** (*the solution in the buret*) that is delivered to the receiving vessel (the beaker shown in the drawing).

In a typical titration, a solution containing one reactant is placed in the receiving vessel. A solution of the other reactant is then added gradually from the buret. (One of the two solutions has a precisely known concentration and is called a **standard solution.**) This addition is continued until something (usually a visual effect, like a color change) signals that the two reactants have been combined in just the right proportions to give a complete reaction.

■ The theory of acid–base indicators is discussed in Chapter 17.

In acid–base titrations, an **acid–base indicator** is used to detect the completion of the reaction by a change in color. Indicators are dyes that have one color in an acidic solution and a different color in a basic solution. Litmus was mentioned earlier. Phenolphthalein is a common indicator for titrations; it changes from colorless to pink when a solution changes from acidic to basic. This color change is very abrupt, and occurs with the addition of only one final drop of the titrant just as the end of the reaction is reached. When we observe the color change, the **end point** has been reached and the addition of titrant is stopped. We then record the total volume of the titrant that's been added to the receiving flask.

Example 5.19
Calculation Involving an Acid–Base Titration

A student prepares a solution of hydrochloric acid that is approximately 0.1 *M* and wants to determine its precise concentration. A 25.00 mL portion of the HCl solution is transferred to a flask, and after a few drops of indicator are added, the HCl solution is titrated with 0.0775 *M* NaOH solution. The titration requires exactly 37.46 mL of the standard NaOH solution to reach the end point. What is the molarity of the HCl solution?

■ **Analysis:** This is really a straightforward stoichiometry calculation involving a chemical reaction. The first step in solving it is to write the balanced equation, which will give us the stoichiometric equivalency between HCl and NaOH. The reaction is an acid–base neutralization, so the product is a salt plus water. Following the procedures developed earlier, the reaction is

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}$$

We have to go from molarity and volume of the NaOH solution to the molarity of the HCl solution. Solving the problem will follow essentially the same route as in Example 5.14 on page 191.

A solution of HCl is titrated with a solution of NaOH using phenolphthalein as the acid-base indicator. The pink color that phenolphthalein has in a basic solution can be seen where a drop of the NaOH solution has entered the HCl solution, to which a few drops of the indicator had been added. *(Michael Watson)*

■ **Assembling the Tools:** Our tools will be the molarity and volume of the NaOH solution (to calculate moles of NaOH that react), the coefficients of the equation (to obtain moles of HCl), and the definition of molarity (to calculate the molarity of the HCl solution from moles of HCl and the volume of the HCl sample taken).

■ **Solution:** From the molarity and volume of the NaOH solution, we calculate the number of moles of NaOH consumed in the titration.

$$0.03746 \ \cancel{\text{L NaOH}} \text{ soln} \times \frac{0.0775 \text{ mol NaOH}}{1.000 \ \cancel{\text{L NaOH soln}}} = 2.903 \times 10^{-3} \text{ mol NaOH}$$

The coefficients in the equation tell us that NaOH and HCl react in a one-to-one mole ratio,

$$2.903 \times 10^{-3} \ \cancel{\text{mol NaOH}} \times \frac{1 \text{ mol HCl}}{1 \ \cancel{\text{mol NaOH}}} = 2.903 \times 10^{-3} \text{ mol HCl}$$

so in this titration, 2.903×10^{-3} mol HCl was in the flask. To calculate the molarity of the HCl, we simply apply the definition of molarity. We take the ratio of the number of moles of HCl that reacted (2.903×10^{-3} mol HCl) to the volume (in liters) of the HCl solution used (25.00 mL, or 0.02500 L).

$$\text{Molarity of HCl soln} = \frac{2.903 \times 10^{-3} \text{ mol HCl}}{0.02500 \text{ L HCl soln}}$$
$$= 0.116\,M \text{ HCl (rounded)}$$

The molarity of the hydrochloric acid is 0.116 *M*. (Note that we've rounded the answer to three significant figures to match the data given in the problem.)

■ **Is the Answer Reasonable?** If the concentrations of the NaOH and HCl were the same, the volumes used would have been equal. However, the volume of the NaOH solution used is larger than the volume of HCl solution. This must mean that the HCl solution is more concentrated than the NaOH solution. The value we obtained, 0.116 *M,* is larger than 0.0775 *M*, so our answer makes sense.

Practice Exercises

5.44 | In a titration, a sample of H_2SO_4 solution having a volume of 15.00 mL required 36.42 mL of 0.147 *M* NaOH solution for *complete* neutralization. What is the molarity of the H_2SO_4 solution? (*Hint:* Check to be sure your chemical equation is correctly written and balanced.)

5.45 | "Stomach acid" is hydrochloric acid. A sample of gastric juice having a volume of 5.00 mL required 11.00 mL of 0.0100 *M* KOH solution for neutralization in a titration. What was the molar concentration of HCl in this fluid? If we assume a density of 1.00 g $\mathrm{mL^{-1}}$ for the fluid, what was the percentage by weight of HCl?

Multi-Concept Problems

The worked examples we've provided so far have been relatively simple, and each has focused on one topic or concept. However, in life and in chemistry, problems are not always that simple. Often they involve multiple concepts that are not immediately obvious, so it is difficult to see how to proceed. Although each problem is unique, there is a general strategy you can learn to apply. The key is realizing that almost all difficult problems can be broken down into some set of simpler tasks that you already know how to do. In fact, in real-life problems, the analysis will sometimes reveal tasks that you have not yet learned how to accomplish and point the way to learning new concepts or tools.

In the *Analyzing and Solving Multi-Concept Problems* section in this and subsequent chapters, our approach will be to look at the big picture first and deal with the details later. The goal will be to break the problem down into manageable parts. There is no simple "formula" for doing this, so don't be discouraged if solving these kinds of problems takes some considerable thought. You should also realize that with complex problems there is often more than one path to the solution. As you study the examples we provide, you may see an alternative way to arrive at the answer. As long as the reasoning is sound and leads to the same answer as ours, you are to be applauded!

Finally, by way of assurance, keep in mind that none of the multi-concept problems you encounter in this text will involve concepts that have not been previously discussed.

Analyzing and Solving Multi-Concept Problems

Milk of magnesia is a suspension of $Mg(OH)_2$ in water. It can be made by adding a base to a solution containing Mg^{2+}. Suppose that 40.0 mL of 0.200 *M* NaOH solution is added to 25.0 mL of 0.300 *M* $MgCl_2$ solution. What mass of $Mg(OH)_2$ will be formed, and what will be the concentrations of the ions in the solution after the reaction is complete?

Analysis: Our goal here is to break the problem down into parts that we already know how to solve. The approach is to read the problem carefully and extract from it the various pieces to the puzzle.

First, we're dealing with the stoichiometry of a chemical reaction, so we know we're going to need a balanced chemical equation. We will also need to determine the concentrations of ions, so we will have to be prepared to write an ionic equation, or at least to take into account the dissociation of each solute. These are things you know how to do, so we have that figured out.

Notice that we've been given the volume and molarity for *both* solutions. By now, you should realize that volume and molarity give us moles, so in effect *we have been given the number of moles of two reactants*. This means we have a limiting reactant problem. You learned how to solve this kind of problem in Chapter 4, so working this part of the problem isn't anything new.

PHILLIPS'
MILK OF MAGNESIA

Creamy milk of magnesia is an aqueous suspension of magnesium hydroxide. *(Robert Capece)*

The problem also asks for the concentrations of the ions in the final mixture. The easiest way to find the answers here is to determine the number of moles of each of the ions present before and after the reaction, and then divide the latter by the total final volume of solution to calculate the molar concentrations. Because this is an ionic reaction, two of the ions will be reactants. One will be completely used up, but some of the other will be left over, and we will have to calculate how much. The other two ions are spectator ions and their amounts will not change.

At this point, we have a broad outline of what we have to do. To further clarify our thinking, let's refine and summarize each part so we can select appropriate tools to accomplish our tasks.

Part 1: Write a balanced molecular equation and then convert it to an ionic equation. (This comes first because all the rest of the reasoning is based on the equation.)

Part 2: Calculate the number of moles of each ion present before reaction, determine the limiting reactant, and then use it to calculate the moles and grams of $Mg(OH)_2$ formed.

Part 3: We already know the moles of the spectator ions from Part 2, but we have to calculate the moles of unreacted Mg^{2+} or OH^-. We also need to determine the total volume of the mixture and then calculate the molarities of the ions.

PART 1

Assembling the Tools We need to set up a metathesis equation and balance it. We follow the procedure developed earlier, making use of the solubility rules.

Solution

The balanced molecular equation for the reaction is

$$\mathrm{MgCl_2}(aq) + \mathrm{2NaOH}(aq) \longrightarrow \mathrm{Mg(OH)_2}(s) + \mathrm{2NaCl}(aq)$$

from which we construct the ionic and net ionic equations.

$$\mathrm{Mg^{2+}}(aq) + \mathrm{2Cl^-}(aq) + \mathrm{2Na^+}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{Mg(OH)_2}(s) + \mathrm{2Na^+}(aq) + \mathrm{2Cl^-}(aq)$$

$$\mathrm{Mg^{2+}}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{Mg(OH)_2}(s)$$

These are the equations we will use in Part 2.

PART 2

Assembling the Tools For each reactant solution,

$$\text{molarity} \times \text{volume(L)} = \text{moles of solute}$$

The chemical formulas of the reactants will be used to find the number of moles of each ion prior to reaction. The method of finding the limiting reactant developed in Chapter 4 will be applied. A tool we will use is the set of coefficients in the equation, which relates moles of the reactants and product. The molar mass tool will be used to convert moles of $\mathrm{Mg(OH)_2}$ to grams.

$$58.31 \text{ g } \mathrm{Mg(OH)_2} = 1 \text{ mol } \mathrm{Mg(OH)_2}$$

Solution Let's begin by determining the number of moles of NaOH and $\mathrm{MgCl_2}$ supplied by the volumes of their solutions. The conversion factors are taken from their molarities: 0.200 *M* NaOH and 0.300 *M* $\mathrm{MgCl_2}$.

$$0.0400\ \cancel{\text{L NaOH soln}} \times \frac{0.200\ \text{mol NaOH}}{1.00\ \cancel{\text{L NaOH soln}}} = 8.00 \times 10^{-3}\ \text{mol NaOH}$$

$$0.0250\ \cancel{\text{L MgCl}_2\text{ soln}} \times \frac{0.300\ \text{mol MgCl}_2}{1.00\ \cancel{\text{L MgCl}_2\text{ soln}}} = 7.50 \times 10^{-3}\ \text{mol MgCl}_2$$

From this information, we obtain the number of moles of each ion present *before* any reaction occurs. In doing this, notice that we take into account that 1 mol of $\mathrm{MgCl_2}$ gives 2 mol $\mathrm{Cl^-}$. Here is a summary of the data.

Moles of Ions before Reaction

$\mathrm{Mg^{2+}}$	7.50×10^{-3} mol	$\mathrm{Cl^-}$	15.0×10^{-3} mol
$\mathrm{Na^+}$	8.00×10^{-3} mol	$\mathrm{OH^-}$	8.00×10^{-3} mol

Now we refer to the net ionic equation, where we see that only $\mathrm{Mg^{2+}}$ and $\mathrm{OH^-}$ react. From the coefficients of the equation,

$$1\ \text{mol}\ \mathrm{Mg^{2+}} \Leftrightarrow 2\ \text{mol}\ \mathrm{OH^-}$$

This means that 7.50×10^{-3} mol $\mathrm{Mg^{2+}}$ (the amount of $\mathrm{Mg^{2+}}$ *available*) would require 15.0×10^{-3} mol $\mathrm{OH^-}$. But we have only 8.00×10^{-3} mol $\mathrm{OH^-}$. Insufficient $\mathrm{OH^-}$ is available to react with all of the $\mathrm{Mg^{2+}}$, so $\mathrm{OH^-}$ must be the limiting reactant. Therefore, all of the $\mathrm{OH^-}$ will be used up and some $\mathrm{Mg^{2+}}$ will be unreacted. The amount of $\mathrm{Mg^{2+}}$ that *does* react to form $\mathrm{Mg(OH)_2}$ can be found as follows.

$$8.00 \times 10^{-3}\ \cancel{\text{mol OH}^-} \times \frac{1\ \text{mol Mg}^{2+}}{2\ \cancel{\text{mol OH}^-}} = 4.00 \times 10^{-3}\ \text{mol Mg}^{2+}$$

(This amount reacts.)

One mole of Mg^{2+} gives 1 mole of $Mg(OH)_2$. Therefore, the amount of $Mg(OH)_2$ that forms is

$$4.00 \times 10^{-3}\ \cancel{\text{mol Mg}^{2+}} \times \frac{1\ \cancel{\text{mol Mg(OH)}_2}}{1\ \cancel{\text{mol Mg}^{2+}}} \times \frac{58.32\ \text{g Mg(OH)}_2}{1\ \cancel{\text{mol Mg(OH)}_2}} = 0.233\ \text{g Mg(OH)}_2$$

The reaction mixture will produce 0.223 g $Mg(OH)_2$.

PART 3

Assembling the Tools To calculate the concentrations of the ions, we can use the number of moles of each present in the final mixture divided by the *total volume* of the solution. This tool is the defining equation for molarity,

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in L}}$$

Solution Let's begin by tabulating the number of moles of each ion left in the mixture *after* the reaction is complete. For Mg^{2+}, the amount remaining equals the initial number of moles minus the moles that react (which we found in Part 2). Let's put all of the numbers into one table to make them easier to understand.

Ion	Moles Present before Reaction	Moles That React	Moles Present after Reaction
Mg^{2+}	7.50×10^{-3} mol	4.00×10^{-3} mol	3.50×10^{-3} mol
Cl^-	15.0×10^{-3} mol	0.00 mol	15.0×10^{-3} mol
Na^+	8.00×10^{-3} mol	0.00 mol	8.00×10^{-3} mol
OH^-	8.00×10^{-3} mol	8.00×10^{-3} mol	0.00 mol

The problem asks for the concentrations of the ions in the final reaction mixture, so we must now divide each quantity in the last column by the *total volume of the final solution* (40.0 mL + 25.0 mL = 65.0 mL). This volume must be expressed in liters (0.0650 L). For example, for Mg^{2+}, its concentration is

$$\frac{3.50 \times 10^{-3}\ \text{mol Mg}^{2+}}{0.0650\ \text{L soln}} = 0.0538\, M\ \text{Mg}^{2+}$$

Performing similar calculations for the other ions gives the following;

Concentrations of Ions after Reaction

Mg^{2+}	0.0538 *M*	Cl^-	0.231 *M*
Na^+	0.123 *M*	OH^-	0.00 *M*

Are the Answers Reasonable? All the reasoning we've done seems to be correct, which is reassuring. For the amount of $Mg(OH)_2$ that forms, 0.001 mol would weigh approximately 0.06 g, so 0.004 mol would weigh 0.24 g. Our answer, 0.233 g $Mg(OH)_2$, is reasonable. The final concentrations of the spectator ions are lower than the initial concentrations, so that makes sense, too, because of the dilution effect.

Summary

Solution Vocabulary. A **solution** is a homogeneous mixture in which one or more **solutes** are dissolved in a **solvent**. A solution may be **dilute** or **concentrated**, depending on the amount of solute dissolved in a given amount of solvent. **Concentration** (e.g., **percentage concentration**) is a ratio of the amount of solute to either the amount of solvent or the amount of solution. The amount of solute required to give a **saturated** solution at a given temperature is called the solute's **solubility**. **Unsaturated** solutions will dissolve more solute, but **supersaturated** solutions are unstable and tend to give a **precipitate**.

Electrolytes. Substances that **dissociate** or **ionize** in water to produce cations and anions are **electrolytes**; those that do not are called **nonelectrolytes**. Electrolytes include salts and metal hydroxides as well as molecular acids and bases that ionize by reaction with water. In water, ionic compounds are completely dissociated into ions and are **strong electrolytes**.

Ionic and Net Ionic Equations. Reactions that occur in solution between ions are called **ionic reactions**. Solutions of soluble strong electrolytes often yield an insoluble product that appears as a **precipitate**. Equations for these reactions can be written in three different ways. In **molecular equations**, complete formulas for all reactants and products are used. In an **ionic equation**, soluble strong electrolytes are written in dissociated (ionized) form; "molecular" formulas are used for solids and weak electrolytes. A **net ionic equation** is obtained by eliminating **spectator ions** from the ionic equation, and such an equation allows us to identify other combinations of reactants that give the same net reaction. An ionic or net ionic equation is balanced only if both atoms *and* net charge are balanced.

Acids and Bases. An **acid** is a substance that produces hydronium ions, H_3O^+, when dissolved in water, and a **base** produces hydroxide ions, OH^-, when dissolved in water. The oxides of nonmetals are generally **acidic anhydrides** and react with water to give acids. Metal oxides are usually **basic anhydrides** because they tend to react with water to give metal hydroxides or bases.

Strong acids and **strong bases** are also strong electrolytes. **Weak acids** and **weak bases** are **weak electrolytes**, which are incompletely ionized in water. In a solution of a weak electrolyte there is a **chemical equilibrium (dynamic equilibrium)** between the non-ionized molecules of the solute and the ions formed by the reaction of the solute with water.

Predicting Metathesis Reactions. **Metathesis** or **double replacement** reactions take place when anions and cations of two salts change partners. A metathesis reaction will occur if there is a net ionic equation. This happens if (1) a precipitate forms from soluble reactants, (2) an acid-base neutralization occurs, (3) a gas is formed, or (4) a weak electrolyte forms from soluble strong electrolytes. You should learn the **solubility rules** (Table 5.1), and remember that all salts are strong electrolytes. All strong acids and bases are strong electrolytes, too. Strong acids react with strong bases in neutralization reactions to produce a salt and water. Acids react with insoluble oxides and hydroxides to form water and the corresponding salt. Many acid–base neutralization reactions can be viewed as a type of metathesis reaction in which one product is water. Be sure to learn the reactions that produce gases in metathesis reactions, which are listed in Table 5.2.

Molar Concentration, Dilution, and Solution Stoichiometry. **Molarity** is the ratio of moles of solute to liters of solution. Molarity provides two conversion factors relating moles of solute and the volume of a solution.

$$\frac{\text{mol solute}}{1\text{ L soln}} \quad \text{and} \quad \frac{1\text{ L soln}}{\text{mol solute}}$$

Concentrated solutions of known molarity can be diluted quantitatively using volumetric glassware such as pipets and volumetric flasks. When a solution is diluted by adding solvent, the amount of solute doesn't change but the concentration decreases.

In ionic reactions, the concentrations of the ions in a solution of a salt can be derived from the molar concentration of the salt, taking into account the number of ions formed per formula unit of the salt.

Titration is a technique used to make quantitative measurements of the amounts of solutions needed to obtain a complete reaction. The apparatus is a long graduated tube called a **buret** that has a **stopcock** at the bottom, which is used to control the flow of **titrant**. In an acid–base titration, the **end point** is normally detected visually using an **acid–base indicator**. A color change indicates complete reaction, at which time the addition of titrant is stopped and the volume added is recorded.

Tools for Problem Solving The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Criteria for a balanced ionic equation (page 164)

To be balanced, an equation that includes the formulas of ions must satisfy the following two criteria: (1) the number of atoms of each kind must be the same on both sides of the equation, and (2) the net electrical charge shown on each side of the equation must be the same.

Ionization of an acid in water (page 165)

Equation 5.2 describes how an acid reacts with water to form hydronium ion plus an anion.

$$\mathrm{H}A + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + A^-$$

Use this tool to write equations for the ionizations of acids and to determine the formulas of the anions formed when the acid molecules lose H^+. The equation also applies to acid anions such as HSO_4^-, which gives SO_4^{2-} when it loses an H^+. Often H_2O is omitted from the equation and the hydronium ion is abbreviated as H^+.

Ionization of a molecular base in water (page 165)

Equation 5.3 describes how molecules of a molecular base acquire H^+ from H_2O to form a cation plus a hydroxide ion.

$$B + \mathrm{H_2O} \longrightarrow B\mathrm{H^+} + \mathrm{OH^-}$$

Use this tool to write equations for the ionizations of bases and to determine the formula of the cation formed when a base molecule gains an H^+. *Molecular bases are weak and are not completely ionized.*

List of strong acids (page 170)

Formulas of the most common strong acids are given here. If you learn this list and encounter an acid that's *not* on the list, you can assume it is a weak acid. The most common strong acids are HCl, HNO_3, and H_2SO_4. *Remember that strong acids are completely ionized in water.*

Acid and anion names (page 173)

This relationship helps us remember the names of acids and anions.

Acid ends in *-ic*	Anion ends in *-ate*
Acid ends in *-ous*	Anion ends in *-ite*

Predicting net ionic equations (page 175)

A net ionic equation will exist and a reaction will occur when:

- A precipitate is formed from a mixture of soluble reactants.
- An acid reacts with a base. *This includes strong or weak acids reacting with strong or weak bases or insoluble metal hydroxides or oxides.*
- A weak electrolyte is formed from a mixture of strong electrolytes.
- A gas is formed from a mixture of reactants.

These criteria are tools to determine whether or not a net reaction will occur in a solution.

Solubility rules (page 176)

The rules in Table 5.1 serve as the tool we use to determine whether a particular salt is soluble in water. (If a salt is soluble, it's completely dissociated into ions.) They also serve as a tool to help predict the course of metathesis reactions.

Gases formed in metathesis reactions (page 181)

Use Table 5.2 as a tool to help predict the outcome of metathesis reactions. The most common gas formed in such reactions is CO_2, which comes from the reaction of an acid with a carbonate or bicarbonate.

Synthesis by metathesis (page 184)

Useful guidelines to use when selecting reactants in the synthesis of a salt are as follows:

1. Start with soluble reactants if the desired product is an insoluble salt.

2. Use an acid–base reaction or a reaction of an acid with a metal carbonate if the desired product is soluble in water. This works best if the metal hydroxide or oxide, or the metal carbonate, is insoluble in water.

Molarity (page 185)

Molarity provides the connection between moles of a solute and the volume of its solution. The definition serves as a tool for calculating molarity from values of moles of solute and volume of solution (in liters).

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molarity is the tool we use to write an equivalence between moles of solute and volume of solution, from which appropriate conversion factors can be formed.

Molarity times volume gives moles (page 187)

For any problem in which you're given both molarity and volume of a solution of a substance, you can always calculate the number of moles of the substance.

$$\text{molarity} \times \text{volume (L)} = \text{moles of solute}$$

Recognizing this relationship is very important when working stoichiometry problems involving solutions.

Dilution equation (page 189)

Equation 5.6 is the tool we use for working dilution problems.

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}}$$

The volume units must be the same on both sides of the equation.

Molarity of ions in a salt solution (page 193)

When using a net ionic equation to work stoichiometry problems, we need the concentrations of the ions in the solutions. *The concentration of a particular ion equals the concentration of the salt multiplied by the number of ions of that kind in one formula unit of the salt.*

Paths through stoichiometry problems

TOOLS

Paths through stoichiometry problems

In this chapter you encountered another way that the data in stoichiometry problems are presented. Figure 5.27 gives an overview of the various paths through problems that involve chemical reactions. All funnel through the coefficients of the balanced chemical equation as the means to convert from moles of one substance to moles of another. The starting and finishing quantities can be moles, grams, or volumes of solutions of known molarity.

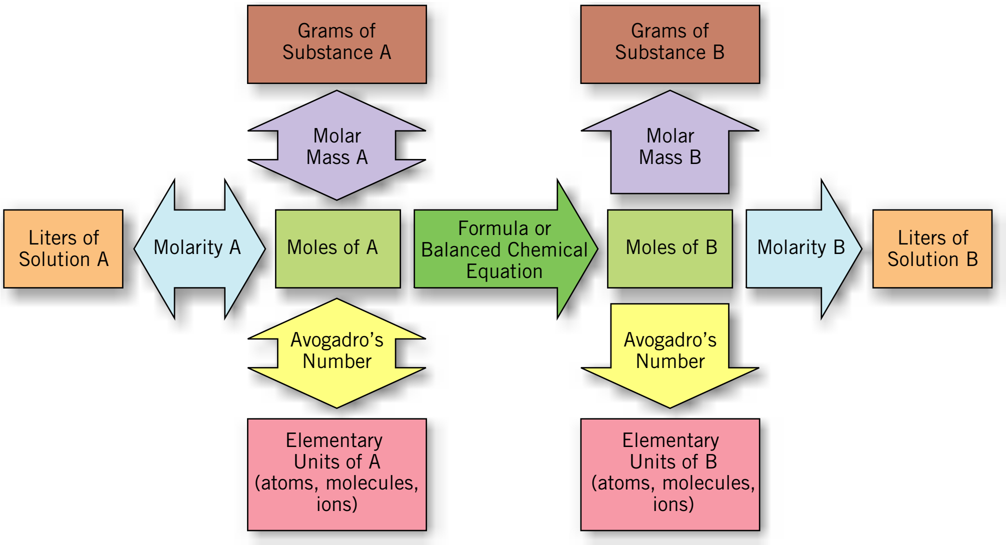

Grams of Substance A
Grams of Substance B
Molar Mass A
Molar Mass B
Liters of Solution A
Molarity A
Moles of A
Formula or Balanced Chemical Equation
Moles of B
Molarity B
Liters of Solution B
Avogadro's Number
Avogadro's Number
Elementary Units of A (atoms, molecules, ions)
Elementary Units of B (atoms, molecules, ions)

Figure 5.27 | **Paths for working stoichiometry problems involving chemical reactions.** The critical step is the conversion between moles of one substance and moles of another using the coefficients of the balanced chemical equation or the subscripts in a chemical formula. We can calculate moles in several ways: from numbers of atomic-sized formula units, and from laboratory units of grams or the volumes of solutions of known molarities. Similarly, we can present the answer either in moles, grams, number of formula units, or a volume of solution of known molarity.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Solution Terminology

5.1 Define the following: **(a)** solvent, **(b)** solute, **(c)** concentration.

5.2 Define the following: **(a)** concentrated, **(b)** dilute, **(c)** saturated, **(d)** unsaturated, **(e)** supersaturated, **(f)** solubility.

5.3 Why are chemical reactions often carried out using solutions?

5.4 Describe what will happen if a crystal of sugar is added to **(a)** a saturated sugar solution, **(b)** a supersaturated solution of sugar, and **(c)** an unsaturated solution of sugar.

5.5 What is the meaning of the term *precipitate*? What condition must exist for a precipitate to form spontaneously in a solution?

Electrolytes

5.6 Which of the following compounds are likely to be electrolytes and which are likely to be nonelectrolytes? $CuBr_2$, $C_{12}H_{22}O_{11}$, CH_3OH, iron(II) chloride, $(NH_4)_2SO_4$.

5.7 Why is an electrolyte able to conduct electricity while a nonelectrolyte cannot? What does it mean when we say that an ion is "hydrated?"

5.8 Define "dissociation" as it applies to ionic compounds that dissolve in water.

5.9 Write equations for the dissociation of the following in water: **(a)** $CaCl_2$, **(b)** $(NH_4)_2SO_4$, **(c)** sodium acetate, **(d)** copper(II) perchlorate.

Ionic Reactions

5.10 The following equation shows the formation of cobalt(II) hydroxide, a compound used to improve the drying properties of lithographic inks.

$$Co^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$$

Which are the spectator ions? Write the net ionic equation.

5.11 How can you tell that the following is a net ionic equation?

$$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$$

5.12 What two conditions must be fulfilled by a balanced ionic equation? The following equation is not balanced. How do we know? Find the errors and fix them.

$$3Co^{3+}(aq) + 2HPO_4^{2-}(aq) \longrightarrow Co_3(PO_4)_2(s) + 2H^+(aq)$$

Acids, Bases, and Their Reactions

5.13 Give two general properties of an acid. Give two general properties of a base.

5.14 If you believed a solution was basic, which color litmus paper (blue or pink) would you use to test the solution to see whether you were correct? What would you observe if you've selected correctly? Why would the other color litmus paper not lead to a conclusive result?

5.15 How did Arrhenius define an acid and a base?

5.16 Which of the following undergo dissociation in water? Which undergo ionization? **(a)** NaOH, **(b)** HNO_3, **(c)** NH_3, **(d)** H_2SO_4

5.17 Which of the following would yield an acidic solution when they react with water? Which would give a basic solution? **(a)** P_4O_{10}, **(b)** K_2O, **(c)** SeO_3, **(d)** Cl_2O_7

5.18 What is a *dynamic equilibrium*? Using acetic acid as an example, describe why all the $HC_2H_3O_2$ molecules are not ionized in water.

5.19 Why don't we use double arrows in the equation for the reaction of a strong acid with water?

5.20 Which of the following are strong acids? **(a)** HCN, **(b)** HNO_3, **(c)** H_2SO_3, **(d)** HCl, **(e)** $HCHO_2$, **(f)** HNO_2

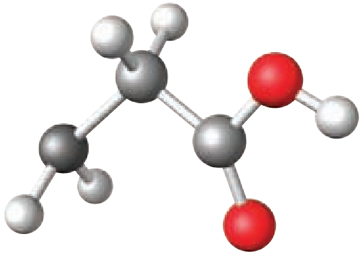
5.21 Which of the following produce a strongly basic solution when dissolved in water? **(a)** C_5H_5N, **(b)** $Ba(OH)_2$ **(c)** KOH, **(d)** $C_6H_5NH_2$, **(e)** Cs_2O, **(f)** N_2O_5

5.22 Methylamine, CH_3NH_2, reacts with hydronium ions in very much the same manner as ammonia.

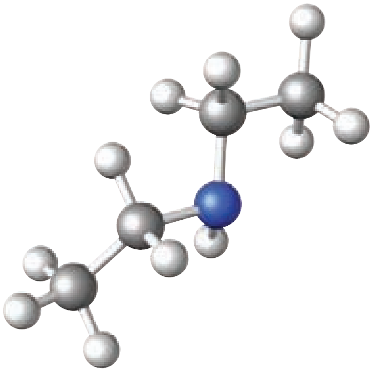
$$CH_3NH_2(aq) + H_3O^+(aq) \longrightarrow CH_3NH_3^+(aq) + H_2O$$

On the basis of what you have learned so far in this course, sketch the molecular structures of CH_3NH_2 and $CH_3NH_3^+$ (the methylammonium ion).

5.23 A student was shown the structure of a molecule of propanoic acid (an organic acid similar to acetic acid) and was asked to draw the structure of the ion formed when the acid underwent ionization in water. Below is the structure the student drew. What is wrong with the structure, and what would you do to correct it?



5.24 Would the molecule shown below be acidic or basic in water? What would you do to the structure to show what happens when the substance reacts with water? Write an equation for the ionization of this compound in water. (The compound is a weak electrolyte.)



Nomenclature of Acids and Bases

5.25 Name the following: **(a)** $H_2Se(g)$, **(b)** $H_2Se(aq)$

5.26 Iodine, like chlorine, forms several acids. What are the names of the following? **(a)** HIO_4, **(b)** HIO_3, **(c)** HIO_2 **(d)** HIO, **(e)** HI

5.27 For the acids in the preceding question, **(a)** write the formulas and, **(b)** name the ions formed by removing a hydrogen ion (H^+) from each acid.

5.28 Write the formula for **(a)** chromic acid, **(b)** carbonic acid and **(c)** oxalic acid. (*Hint:* Check the table of polyatomic ions.)

5.29 Name the following acid salts: **(a)** $NaHCO_3$, **(b)** KH_2PO_4, **(c)** $(NH_4)_2HPO_4$.

5.30 Write the formulas for all the acid salts that could be formed from the reaction of NaOH with the acid H_3PO_4.

5.31 Name the following oxoacids and give the names and formulas of the salts formed from them by neutralization with NaOH: **(a)** HOCl, **(b)** HIO_2, **(c)** $HBrO_3$, **(d)** $HClO_4$.

5.32 The formula for the arsenate ion is AsO_4^{3-}. What is the formula for arsenous acid?

5.33 Butanoic acid (also called butyric acid), $HC_4H_7O_2$, gives rancid butter its bad odor. What is the name of the salt $NaC_4H_7O_2$?

5.34 Calcium propanoate, $Ca(C_3H_5O_2)_2$, is used in baked foods as a preservative and to prevent the growth of mold. Based on the name of the salt, what is the name of the acid $HC_3H_5O_2$?

Predicting Ionic Reactions

5.35 What factors lead to the existence of a net ionic equation in a reaction between ions?

5.36 What is another name for a *metathesis reaction*?

5.37 Silver bromide is "insoluble." What does this mean about the concentrations of Ag^+ and Br^- in a saturated solution of AgBr? Explain why a precipitate of AgBr forms when solutions of the soluble salts $AgNO_3$ and NaBr are mixed.

5.38 If a solution of sodium phosphate (also known as trisodium phosphate, or TSP), Na_3PO_4, is poured into seawater, precipitates of calcium phosphate and magnesium phosphate are formed. (Magnesium and calcium ions are among the principal ions found in seawater.) Write net ionic equations for these reactions.

5.39 Washing soda is $Na_2CO_3 \cdot 10H_2O$. Explain, using chemical equations, how this substance is able to remove Ca^{2+} ions from "hard water."

5.40 With which of the following will the weak acid $HCHO_2$ react? For those with which there is a reaction, write the formulas of the products. **(a)** KOH **(b)** MgO **(c)** NH_3

5.41 Suppose you suspected that a certain solution contained ammonium ions. What simple chemical test could you perform that would tell you whether your suspicion was correct?

5.42 What gas is formed if HCl is added to **(a)** $NaHCO_3$, **(b)** Na_2S, and **(c)** potassium sulfite?

Molarity and Dilution

5.43 What is the definition of molarity? Show that the ratio of millimoles (mmol) to milliliters (mL) is equivalent to the ratio of moles to liters.

5.44 A solution is labeled 0.25 *M* HCl. Construct two conversion factors that relate moles of HCl to the volume of solution expressed in liters.

5.45 When the units *molarity* and *liter* are multiplied, what are the resulting units?

5.46 When a solution labeled 0.50 *M* HNO_3 is diluted with water to give 0.25 *M* HNO_3, what happens to the number of moles of HNO_3 in the solution?

5.47 Two solutions, A and B, are labeled "0.100 *M* $CaCl_2$" and "0.200 *M* $CaCl_2$," respectively. Both solutions contain the same number of moles of $CaCl_2$. If solution A has a volume of 50.0 mL, what is the volume of solution B?

Chemical Analyses and Titrations

5.48 What is the difference between a qualitative analysis and a quantitative analysis?

5.49 Describe each of the following: **(a)** buret, **(b)** titration, **(c)** titrant, and **(d)** end point.

5.50 What is the function of an indicator in a titration? What color is phenolphthalein in **(a)** an acidic solution and **(b)** a basic solution?

Review Problems

Ionic Reactions

5.51 Write balanced ionic and net ionic equations for these reactions.

(a) $(NH_4)_2CO_3(aq) + MgCl_2(aq) \longrightarrow NH_4Cl(aq) + MgCO_3(s)$

(b) $CuCl_2(aq) + NaOH(aq) \longrightarrow Cu(OH)_2(s) + NaCl(aq)$

(c) $FeSO_4(aq) + Na_3PO_4(aq) \longrightarrow Fe_3(PO_4)_2(s) + Na_2SO_4(aq)$

(d) $AgC_2H_3O_2(aq) + NiCl_2(aq) \longrightarrow AgCl(s) + Ni(C_2H_3O_2)_2(aq)$

OH **5.52** Write balanced ionic and net ionic equations for these reactions.

(a) $CuSO_4(aq) + BaCl_2(aq) \longrightarrow CuCl_2(aq) + BaSO_4(s)$

(b) $Fe(NO_3)_3(aq) + LiOH(aq) \longrightarrow LiNO_3(aq) + Fe(OH)_3(s)$

(c) $Na_3PO_4(aq) + CaCl_2(aq) \longrightarrow Ca_3(PO_4)_2(s) + NaCl(aq)$

(d) $Na_2S(aq) + AgC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(aq) + Ag_2S(s)$

Acids and Bases as Electrolytes

5.53 Pure $HClO_4$ is molecular. In water it is a strong acid. Write an equation for its ionization in water.

5.54 Hydrogen bromide is a molecular substance that is a strong acid in water. Write an equation for its ionization in water.

OH **5.55** Hydrazine is a toxic substance that can form when household ammonia is mixed with a bleach such as Clorox. Its formula is N_2H_4, and it is a weak base. Write a chemical equation showing its reaction with water.

5.56 Pyridine, C_5H_5N, is a fishy-smelling compound used as an intermediate in making insecticides. It is a weak base. Write a chemical equation showing its reaction with water.

5.57 Nitrous acid, HNO_2, is a weak acid that can form when sodium nitrite, a meat preservative, reacts with stomach acid (HCl). Write an equation showing the ionization of HNO_2 in water.

5.58 Pentanoic acid, $HC_5H_9O_2$, is found in a plant called valerian, which cats seem to like almost as much as catnip. Also called valeric acid, it is a weak acid. Write an equation showing its reaction with water.

5.59 Carbonic acid is a weak diprotic acid formed in rainwater as it passes through the atmosphere and dissolves carbon dioxide. Write chemical equations for the equilibria involved in the stepwise ionization of carbonic acid in water.

5.60 Phosphoric acid is a weak acid found in some soft drinks. It undergoes ionization in three steps. Write chemical equations for the equilibria involved in each of these reactions.

Metathesis Reactions

5.61 Aqueous solutions of sodium sulfide and copper(II) nitrate are mixed. A precipitate of copper(II) sulfide forms at once. The solution that remains contains sodium nitrate. Write the molecular, ionic, and net ionic equations for this reaction.

5.62 If an aqueous solution of iron(III) sulfate (a compound used in dyeing textiles and also for etching aluminum) is mixed with a solution of barium chloride, a precipitate of barium sulfate forms and the solution that remains contains iron(III) chloride. Write the molecular, ionic, and net ionic equations for this reaction.

5.63 Use the solubility rules to decide which of the following compounds are *soluble* in water.

(a) $Ca(NO_3)_2$

(b) $FeCl_2$

(c) $Ni(OH)_2$

(d) silver nitrate

(e) barium sulfate

(f) copper(II) carbonate

5.64 Predict which of the following compounds are *soluble* in water.

(a) $HgBr_2$

(b) $Sr(NO_3)_2$

(c) Hg_2Br_2

(d) ammonium phosphate

(e) lead(II) iodide

(f) lead(II) acetate

5.65 Complete and balance the following molecular equations, being careful to apply the solubility rules. Write balanced ionic and net ionic equations for the reactions.

(a) $FeSO_4(aq) + K_3PO_4(aq) \longrightarrow$

(b) $AgC_2H_3O_2(aq) + AlCl_3(aq) \longrightarrow$

(c) chromium(III) chloride + barium hydroxide ⟶

5.66 Complete and balance the following molecular equations, being careful to apply the solubility rules. Write balanced ionic and net ionic equations for the reactions.

(a) $Fe(NO_3)_3(aq) + KOH(aq) \longrightarrow$

(b) $Na_3PO_4(aq) + SrCl_2(aq) \longrightarrow$

(c) lead(II) acetate + ammonium sulfate ⟶

Acid–Base Neutralization Reactions

5.67 Complete and balance the following equations. For each, write the molecular, ionic, and net ionic equations. (All the products are soluble in water.)

(a) $Ca(OH)_2(aq) + HNO_3(aq) \longrightarrow$

(b) $Al_2O_3(s) + HCl(aq) \longrightarrow$

(c) $Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow$

5.68 Complete and balance the following equations. For each, write the molecular, ionic, and net ionic equations. (All the products are soluble in water.)

(a) $HC_2H_3O_2(aq) + Mg(OH)_2(s) \longrightarrow$

(b) $HClO_4(aq) + NH_3(aq) \longrightarrow$

(c) $H_2CO_3(aq) + NH_3(aq) \longrightarrow$

5.69 How would the electrical conductivity of a solution of barium hydroxide change as a solution of sulfuric acid is added slowly to it? Use a net ionic equation to justify your answer.

5.70 How would the electrical conductivity of a solution of acetic acid change as a solution of ammonia is added slowly to it? Use a net ionic equation to justify your answer.

Ionic Reactions That Produce Gases

5.71 Write balanced net ionic equations for the reaction between:

(a) $HNO_3(aq) + K_2CO_3(aq)$

(b) $Ca(OH)_2(aq) + NH_4NO_3(aq)$

5.72 Write balanced net ionic equations for the reaction between:

(a) $H_2SO_4(aq) + NaHSO_3(aq)$

(b) $HNO_3(aq) + (NH_4)_2CO_3(aq)$

Predicting Ionic Reactions

5.73 Explain why the following reactions take place.

(a) $CrCl_3 + 3NaOH \longrightarrow Cr(OH)_3 + 3NaCl$

(b) $ZnO + 2HBr \longrightarrow ZnBr_2 + H_2O$

OH **5.74** Explain why the following reactions take place.

(a) $MnCO_3 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + CO_2$

(b) $Na_2C_2O_4 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2C_2O_4$

5.75 Complete and balance the molecular, ionic, and net ionic equations for the following reactions.

(a) $HNO_3 + Cr(OH)_3 \longrightarrow$

(b) $HClO_4 + NaOH \longrightarrow$

(c) $Cu(OH)_2 + HC_2H_3O_2 \longrightarrow$

(d) $ZnO + H_2SO_4 \longrightarrow$

5.76 Complete and balance the molecular, ionic, and net ionic equations for the following reactions.

(a) $NaHSO_3 + HBr \longrightarrow$

(b) $(NH_4)_2CO_3 + NaOH \longrightarrow$

(c) $(NH_4)_2CO_3 + Ba(OH)_2 \longrightarrow$

(d) $FeS + HCl \longrightarrow$

ILW **5.77** Write balanced molecular, ionic, and net ionic equations for the following pairs of reactants. If all ions cancel, indicate that no reaction (N.R.) takes place.

(a) sodium sulfite and barium nitrate

(b) formic acid ($HCHO_2$) and potassium carbonate

(c) ammonium bromide and lead(II) acetate

(d) ammonium perchlorate and copper(II) nitrate

5.78 Write balanced molecular, ionic, and net ionic equations for the following pairs of reactants. If all ions cancel, indicate that no reaction (N.R.) takes place.

(a) ammonium sulfide and sodium hydroxide

(b) chromium(III) sulfate and potassium carbonate

(c) silver nitrate and chromium(III) acetate

(d) strontium hydroxide and magnesium chloride

***5.79** Choose reactants that would yield the following net ionic equations. Write molecular equations for each.

(a) $HCO_3^-(aq) + H^+(aq) \longrightarrow H_2O + CO_2(g)$

(b) $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$

(c) $Ba^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow BaSO_3(s)$

(d) $2Ag^+(aq) + S^{2-}(aq) \longrightarrow Ag_2S(s)$

(e) $ZnO(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2O$

***5.80** Suppose that you wanted to prepare copper(II) carbonate by a precipitation reaction involving Cu^{2+} and CO_3^{2-}. Which of the following pairs of reactants could you use as solutes?

(a) $Cu(OH)_2 + Na_2CO_3$

(b) $CuSO_4 + (NH_4)_2CO_3$

(c) $Cu(NO_3)_2 + CaCO_3$

(d) $CuCl_2 + K_2CO_3$

(e) $CuS + NiCO_3$

Molar Concentration

OH **5.81** Calculate the molarity of a solution prepared by dissolving

(a) 4.00 g of sodium hydroxide in a total volume of 100.0 mL of solution.

(b) 16.0 g of calcium chloride in a total volume of 250.0 mL of solution.

5.82 Calculate the molarity of a solution that contains

(a) 3.60 g of sulfuric acid in 450.0 mL of solution.

(b) 2.00×10^{-3} mol iron(II) nitrate in 12.0 mL of solution.

5.83 How many milliliters of 0.265 M $NaC_2H_3O_2$ are needed to supply 14.3 g $NaC_2H_3O_2$?

5.84 How many milliliters of 0.615 M HNO_3 contain 1.67 g HNO_3?

ILW **5.85** Calculate the number of grams of each solute that has to be taken to make each of the following solutions.

(a) 125 mL of 0.200 M NaCl

(b) 250.0 mL of 0.360 M $C_6H_{12}O_6$ (glucose)

(c) 250.0 mL of 0.250 M H_2SO_4

5.86 How many grams of solute are needed to make each of the following solutions?

(a) 250.0 mL of 0.100 M potassium sulfate

(b) 100.0 mL of 0.250 M iron(III) chloride

(c) 500.0 mL of 0.400 M barium acetate

Dilution of Solutions

5.87 If 25.0 mL of 0.56 M H_2SO_4 is diluted to a volume of 125 mL, what is the molarity of the resulting solution?

5.88 A 150 mL sample of 0.450 M HNO_3 is diluted to 450 mL. What is the molarity of the resulting solution?

ILW 5.89 To what volume must 25.0 mL of 18.0 M H_2SO_4 be diluted to produce 1.50 M H_2SO_4?

5.90 To what volume must 50.0 mL of 1.50 M HCl be diluted to produce 0.200 M HCl?

5.91 How many milliliters of water must be added to 150.0 mL of 2.50 M KOH to give a 1.00 M solution? (Assume the volumes are additive.)

5.92 How many milliliters of water must be added to 120.0 mL of 1.50 M HCl to give 1.00 M HCl? (Assume the volumes are additive.)

Concentrations of Ions in Solutions of Electrolytes

5.93 Calculate the number of moles of each of the ions in the following solutions.

(a) 32.3 mL of 0.455 M $CaCl_2$

(b) 50.0 mL of 0.408 M $AlCl_3$

5.94 Calculate the number of moles of each of the ions in the following solutions.

(a) 18.5 mL of 0.402 M $(NH_4)_2CO_3$

(b) 30.0 mL of 0.359 M $Al_2(SO_4)_3$

5.95 Calculate the concentrations of each of the ions in **(a)** 0.25 M $Cr(NO_3)_2$, **(b)** 0.10 M $CuSO_4$, **(c)** 0.16 M Na_3PO_4, **(d)** 0.075 M $Al_2(SO_4)_3$.

5.96 Calculate the concentrations of each of the ions in **(a)** 0.060 M $Ca(OH)_2$, **(b)** 0.15 M $FeCl_3$, **(c)** 0.22 M $Cr_2(SO_4)_3$, **(d)** 0.60 M $(NH_4)_2SO_4$.

5.97 In a solution of $Al_2(SO_4)_3$ the Al^{3+} concentration is 0.125 M. How many grams of $Al_2(SO_4)_3$ are in 50.0 mL of this solution?

5.98 In a solution of $NiCl_2$, the Cl^- concentration is 0.0556 M. How many grams of $NiCl_2$ are in 225 mL of this solution?

Solution Stoichiometry

OH 5.99 How many milliliters of 0.258 M $NiCl_2$ solution are needed to react completely with 20.0 mL of 0.153 M Na_2CO_3 solution? How many grams of $NiCO_3$ will be formed? The reaction is

$$Na_2CO_3(aq) + NiCl_2(aq) \longrightarrow NiCO_3(s) + 2NaCl(aq)$$

5.100 How many milliliters of 0.100 M NaOH are needed to completely neutralize 25.0 mL of 0.250 M $H_2C_4H_4O_6$? The reaction is

$$2NaOH(aq) + H_2C_4H_4O_6(aq) \longrightarrow Na_2C_4H_4O_6(aq) + 2H_2O$$

5.101 What is the molarity of an aqueous solution of potassium hydroxide if 21.34 mL is exactly neutralized by 20.78 mL of 0.116 M HCl? Write and balance the molecular equation for the reaction.

5.102 What is the molarity of an aqueous phosphoric acid solution if 12.88 mL is completely neutralized by 26.04 mL of 0.1024 M NaOH? Write and balance the molecular equation for the reaction.

5.103 Aluminum sulfate, $Al_2(SO_4)_3$, is used in water treatment to remove fine particles suspended in the water. When made basic, a gel-like precipitate forms that removes the fine particles as it settles. In an experiment, a student planned to react $Al_2(SO_4)_3$ with $Ba(OH)_2$. How many grams of $Al_2(SO_4)_3$ are needed to react with 85.0 mL of 0.0500 M $Ba(OH)_2$?

5.104 How many grams of baking soda, $NaHCO_3$, are needed to react with 162 mL of stomach acid having an HCl concentration of 0.052 M?

5.105 How many milliliters of 0.150 M $FeCl_3$ solution are needed to react completely with 20.0 mL of 0.0450 M $AgNO_3$ solution? How many grams of AgCl will be formed? The net ionic equation for the reaction is

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

5.106 How many grams of cobalt(II) chloride are needed to react completely with 60.0 mL of 0.200 M KOH solution? The net ionic equation for the reaction is

$$Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$$

ILW 5.107 Consider the reaction of aluminum chloride with silver acetate. How many milliliters of 0.250 M aluminum chloride would be needed to react completely with 20.0 mL of 0.500 M silver acetate solution? The net ionic equation for the reaction is

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

5.108 How many milliliters of ammonium sulfate solution having a concentration of 0.250 M are needed to react completely with 50.0 mL of 1.00 M sodium hydroxide solution? The net ionic equation for the reaction is

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O$$

***5.109** Suppose that 4.00 g of solid Fe_2O_3 is added to 25.0 mL of 0.500 M HCl solution. What will the concentration of the Fe^{3+} be when all of the HCl has reacted? What mass of Fe_2O_3 will not have reacted?

***5.110** Suppose 3.50 g of solid $Mg(OH)_2$ is added to 30.0 mL of 0.500 M H_2SO_4 solution. What will the concentration of Mg^{2+} be when all of the acid has been neutralized? How many grams of $Mg(OH)_2$ will not have dissolved?

Titrations and Chemical Analyses

5.111 In a titration, 23.25 mL of 0.105 *M* NaOH was needed to react with 21.45 mL of HCl solution. What is the molarity of the acid?

5.112 A 12.5 mL sample of vinegar, containing acetic acid, was titrated using 0.504 *M* NaOH solution. The titration required 20.65 mL of the base.

(a) What was the molar concentration of acetic acid in the vinegar?

(b) Assuming the density of the vinegar is 1.01 g mL^{-1}, what was the percent (by mass) of acetic acid in the vinegar?

ILW OH **5.113** Lactic acid, $HC_3H_5O_3$, is a monoprotic acid that forms when milk sours. An 18.5 mL sample of a solution of lactic acid required 17.25 mL of 0.155 *M* NaOH to reach an end point in a titration. **(a)** How many moles of lactic acid were in the sample? **(b)** How many grams of lactic acid were in the sample?

5.114 Ascorbic acid (vitamin C) is a diprotic acid having the formula $H_2C_6H_6O_6$. A sample of a vitamin supplement was analyzed by titrating a 0.1000 g sample dissolved in water with 0.0200 *M* NaOH. A volume of 15.20 mL of the base was required to completely neutralize the ascorbic acid. What was the percentage by mass of ascorbic acid in the sample?

5.115 A certain lead ore contains the compound $PbCO_3$. A sample of the ore weighing 1.526 g was treated with nitric acid, which dissolved the $PbCO_3$. The resulting solution was filtered from undissolved rock and required 29.22 mL of 0.122 *M* Na_2SO_4 to completely precipitate all of the lead as $PbSO_4$. **(a)** How many moles of lead were in the ore sample? **(b)** How many grams of lead were in the ore sample? **(c)** What is the percentage by mass of lead in the ore?

5.116 An ore of barium contains $BaCO_3$. A 1.542 g sample of the ore was treated with HCl to dissolve the $BaCO_3$. The resulting solution was filtered to remove insoluble material and then treated with H_2SO_4 to precipitate $BaSO_4$. The precipitate was filtered, dried, and found to weigh 1.159 g. What is the percentage by mass of barium in the ore? (Assume all of the barium is precipitated as $BaSO_4$.)

Additional Exercises

***5.117** Suppose that 25.0 mL of 0.440 *M* NaCl is added to 25.0 mL of 0.320 *M* $AgNO_3$.

(a) How many moles of AgCl would precipitate?

(b) What would be the concentrations of each of the ions in the reaction mixture after the reaction?

***5.118** A mixture is prepared by adding 25.0 mL of 0.185 *M* Na_3PO_4 to 34.0 mL of 0.140 *M* $Ca(NO_3)_2$.

(a) What mass of $Ca_3(PO_4)_2$ will be formed?

(b) What will be the concentrations of each of the ions in the mixture after reaction?

5.119 Classify each of the following as a strong electrolyte, weak electrolyte, or nonelectrolyte.

(a) KCl

(b) $C_3H_5(OH)_3$ (glycerin)

(c) NaOH

(d) $C_{12}H_{22}O_{11}$ (sucrose, or table sugar)

(e) $HC_2H_3O_2$ (acetic acid)

(f) CH_3OH (methyl alcohol)

(g) H_2SO_4

(h) NH_3

OH **5.120** Complete the following and write molecule, ionic, and net ionic equations. State whether a net reaction occurs in each case.

(a) $CaCO_3 + HNO_3 \longrightarrow$ **(c)** $FeS + HBr \longrightarrow$

(b) $CaCO_3 + H_2SO_4 \longrightarrow$ **(d)** $KOH + SnCl_2 \longrightarrow$

OH ***5.121** Aspirin is a monoprotic acid called acetylsalicylic acid. Its formula is $HC_9H_7O_4$. A certain pain reliever was analyzed for aspirin by dissolving 0.250 g of it in water and titrating it with 0.0300 *M* KOH solution. The titration required 29.40 mL of base. What is the percentage by weight of aspirin in the drug?

***5.122** In an experiment, 40.0 mL of 0.270 *M* barium hydroxide was mixed with 25.0 mL of 0.330 *M* aluminum sulfate.

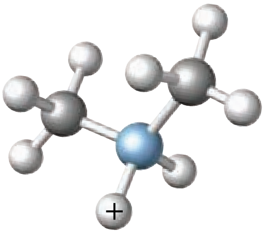
(a) Write the net ionic equation for the reaction that takes place.

(b) What is the total mass of precipitate that forms?

(c) What are the molar concentrations of the ions that remain in the solution after the reaction is complete?

***5.123** How many milliliters of 0.10 *M* HCl must be added to 50.0 mL of 0.40 *M* HCl to give a final solution that has a molarity of 0.25 *M*?

5.124 Write an equation for the reaction of sodium hydroxide with the chloride salt of the cation with the following structure. How many grams of sodium hydroxide are needed to completely react with 12.4 g of the salt?



Multi-Concept Problems

* **5.125** Magnesium sulfate forms a hydrate known as *Epsom salts*. A student dissolved 1.24 g of this hydrate in water and added a barium chloride solution until the precipitation reaction was complete. The precipitate was filtered, dried, and found to weigh 1.174 g. Determine the formula for Epsom salts.

***5.126** Qualitative analysis of an unknown acid found only carbon, hydrogen, and oxygen. In a quantitative analysis, a 10.46 mg sample was burned in oxygen and gave 22.17 mg CO_2 and 3.40 mg H_2O. The molecular mass was determined to be 166 g mol^{-1}. When a 0.1680 g sample of the acid was titrated with 0.1250 M NaOH, the end point was reached after 16.18 mL of the base had been added. **(a)** What is the molecular formula for the acid? **(b)** Is the acid mono-, di-, or triprotic?

***5.127** A mixture was known to contain both KNO_3 and K_2SO_3. To 0.486 g of the mixture, dissolved in enough water to give 50.00 mL of solution, was added 50.00 mL of 0.150 M HCl (an excess of HCl). The reaction mixture was heated to drive off all of the SO_2, and then 25.00 mL of the reaction mixture was titrated with 0.100 M KOH. The titration required 13.11 mL of the KOH solution to reach an end point. What was the percentage by mass of K_2SO_3 in the original mixture of KNO_3 and K_2SO_3?

***5.128** A white substance was known to be either magnesium hydroxide, calcium hydroxide, or zinc oxide. A 1.25 g sample of the substance was mixed with 50.0 mL of water and 100.0 mL of 0.500 M HCl was added. The mixture was stirred, causing all of the sample to dissolve. The excess HCl in the solution required 36.0 mL of 0.200 M NaOH for complete neutralization in a titration. What was the identity of the white substance?

***5.129** A steel cylinder with a diameter of 10.0 cm and a length of 30.0 cm was coated with a thin layer of zinc. The cylinder was dipped briefly in hydrochloric acid, which completely dissolved the coating of zinc, giving Zn^{2+} in the solution. When made basic, the mixture yielded 0.226 g of a $Zn(OH)_2$ precipitate. If a zinc atom occupies an average area of 6.31×10^4 pm^2 on the surface of the cylinder, how many layers of atoms thick was the zinc coating on the cylinder?

Exercises in Critical Thinking

5.130 Compare the advantages and disadvantages of performing a titration using the mass of the sample and titrant rather than the volume.

5.131 What kinds of experiments could you perform to measure the solubility of a substance in water? Describe the procedure you would use and the measurements you would make. What factors would limit the precision of your measurements?

5.132 Describe experiments, both qualitative and quantitative, that you could perform to show that lead chloride is more soluble in water than lead iodide.

5.133 How could you check the accuracy of a 100 mL volumetric flask?

5.134 Suppose a classmate doubted that an equilibrium really exists between acetic acid and its ions in an aqueous solution. What argument would you use to convince the person that such an equilibrium does exist?

5.135 When Arrhenius originally proposed that ions exist in solution, his idea was not well received. Propose another explanation for the conduction of electricity in molten salts and aqueous salt solutions.

5.136 Carbon dioxide is one obvious contributor to excessive global warming. What is your plan for controlling CO_2 emissions? What are the advantages and disadvantages of your plan?

6 Oxidation–Reduction Reactions

Chapter Outline

6.1 | Oxidation–Reduction Reactions

6.2 | Balancing Redox Equations

6.3 | Acids as Oxidizing Agents

6.4 | Redox Reactions of Metals

6.5 | Molecular Oxygen as an Oxidizing Agent

6.6 | Stoichiometry of Redox Reactions

The beautiful, wispy, smoke-like fog that hangs over the Smoky Mountains in Tennessee and North Carolina comes from emissions from the deciduous trees and shrubs native to the mountains.[1] This natural haze is a result of photochemical smog: the compounds emitted by the trees react with sunlight and natural oxidants (compounds that remove electrons from other compounds) to form substances called *carboxylic acids*, which come together to form particles that scatter sunlight and produce a haze. In this chapter we will study reactions that occur by electron transfer—reactions of great importance in our everyday lives. Besides being involved in the formation of smog, these reactions have practical applications that range from the functioning of batteries to the burning of fossil fuels. (Carr Clifton/Minden Pictures, Inc.)

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[1] F. Paulot et al., Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, *Science*, **325**, 730–733.

This Chapter in Context

In Chapter 5 you learned about some important reactions that take place in aqueous solutions. This chapter expands on that knowledge with a discussion of a class of reactions that can be viewed as involving the transfer of one or more electrons from one reactant to another. Our goal is to teach you how to recognize and analyze the changes that occur in these reactions and how to balance equations for reactions that involve electron transfer. You will also learn how to apply the principles of stoichiometry to these reactions and how to predict a type of reaction called single replacement. The reactions discussed here constitute a very broad class with many practical examples that range from combustion to batteries to the metabolism of foods by our bodies. Although we will introduce you to some of them in this chapter, we will wait until Chapter 20 to discuss some of the others.

6.1 | Oxidation–Reduction Reactions

Among the first reactions studied by early scientists were those that involved oxygen. The combustion of fuels and the reactions of metals with oxygen to give oxides were described by the word *oxidation*. The removal of oxygen from metal oxides to give the metals in their elemental forms was described as *reduction*.

■ Oxygen had just been discovered by Joseph Priestley in 1774.

■ The term redox was coined to emphasize that reduction and oxidation must always occur together in chemical reactions.

In 1789, the French chemist Antoine Lavoisier discovered that *combustion* involves the reaction of chemicals in various fuels, like wood and coal, not just with air but specifically with the oxygen in air. Over time, scientists came to realize that such reactions were actually special cases of a much more general phenomenon, one in which electrons are transferred from one substance to another. Collectively, electron transfer reactions came to be called **oxidation–reduction reactions,** or simply **redox reactions**. The term **oxidation** was used to describe the loss of electrons by one reactant, and **reduction** to describe the gain of electrons by another. For example, the reaction between sodium and chlorine to yield sodium chloride involves a loss of electrons by sodium (*oxidation* of sodium) and a gain of electrons by chlorine (*reduction* of chlorine). We can write these changes in equation form including the electrons, which we represent by the symbol e^-.

■ Notice that when we write equations of this type, the electron appears as a "product" if the process is oxidation and as a "reactant" if the process is reduction.

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^- \qquad \text{(oxidation)}$$

$$\mathrm{Cl}_2 + 2e^- \longrightarrow 2\mathrm{Cl}^- \qquad \text{(reduction)}$$

We say that sodium, Na, is oxidized and chlorine, Cl_2, is reduced.

Oxidation and reduction always occur together. No substance is ever oxidized unless something else is reduced, and the total number of electrons lost by one substance is always the same as the total number gained by the other. If this were not true, electrons would appear as a product of the overall reaction, and this is never observed.[2] In the reaction of sodium with chlorine, for example, the overall reaction is

$$2\mathrm{Na} + \mathrm{Cl}_2 \longrightarrow 2\mathrm{NaCl}$$

When two sodium atoms are oxidized, two electrons are lost, which is exactly the number of electrons gained when one Cl_2 molecule is reduced.

■ The *oxidizing agent* causes oxidation to occur by accepting electrons (it gets reduced). The *reducing agent* causes reduction by supplying electrons (it gets oxidized).

For a redox reaction to occur, one substance must accept electrons from the other. The substance that accepts the electrons is called the **oxidizing agent**; it is the agent that allows the other substance to lose electrons and be oxidized. Similarly, the substance that supplies the electrons is called the **reducing agent** because it helps something else to be reduced.

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[2] If electron loss didn't equal electron gain, it would also violate the law of conservation of mass, and that doesn't happen in chemical reactions.

In our example above, sodium serves as a reducing agent when it supplies electrons to chlorine. In the process, sodium is oxidized. Chlorine is an oxidizing agent when it accepts electrons from the sodium, and when that happens, chlorine is reduced to chloride ion. One way to remember this is by the following summary:

> The reducing agent is the substance that is oxidized.
>
> The oxidizing agent is the substance that is reduced.

Redox reactions are very common. They occur in batteries, which are built so that the electrons transferred can pass through some external circuit where they are able to light a flashlight or power an iPod. The metabolism of foods, which supplies our bodies with energy, also occurs by a series of redox reactions. In the Smoky Mountains, the photochemical haze is produced by oxidation of isoprene (emitted by trees) by oxygen in the air. And ordinary household bleach works by oxidizing substances that stain fabrics, making them colorless or easier to remove from the fabric (see Figure 6.1).

REGULAR
CLOROX
BLEACH

Figure 6.1 | **"Chlorine" bleach.** This common household product is a dilute aqueous solution of sodium hypochlorite, NaOCl, which destroys fabric stains by oxidizing them to colorless products. *(OPC, Inc.)*

TOOLS

Oxidizing and reducing agents

Example 6.1
Identifying Oxidation–Reduction

The bright light produced by the reaction between magnesium and oxygen often is used in fireworks displays. The product of the reaction is magnesium oxide, an ionic compound. Which element is oxidized and which is reduced? What are the oxidizing and reducing agents?

Analysis: This question asks us to apply the definitions presented above, so we need to know how the electrons are transferred in the reaction.

Assembling the Tools: As stated, magnesium oxide is an ionic compound. Using the tools you learned in Chapter 3, the locations of the elements in the periodic table tell us that the ions are Mg^{2+} and O^{2-}, so the formula for magnesium oxide is MgO. The reactants are magnesium, Mg, and molecular oxygen, O_2. The equation for the reaction is therefore

$$2Mg + O_2 \longrightarrow 2MgO$$

Now that we have the balanced chemical equation and the formulas of the ions, we can determine how electrons are exchanged and use the definitions of oxidizing and reducing agent as tools to answer the question.

Fireworks display over Washington, D.C. *(Pete Saloutos/Corbis Images)*

Solution: When a magnesium atom becomes a magnesium ion, it must lose two electrons, and they appear in the products when we express the reaction as an equation.

$$Mg \longrightarrow Mg^{2+} + 2e^-$$

By losing electrons, *magnesium is oxidized, so it is the reducing agent.*

When oxygen reacts to yield O^{2-} ions, each oxygen atom must gain two electrons, so an O_2 molecule must gain four electrons; these electrons appear on the reactant side of the equation.

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

By gaining electrons, *O_2 is reduced* and *must be the oxidizing agent.*

■ **Is the Answer Reasonable?** There are two things we can do to check our answers. First, we can check to be sure that we've placed electrons on the correct sides of the equations. As with ionic equations, *the number of atoms of each kind and the net charge must be the same on both sides*. We see that this is true for both equations. (If we had placed the electrons on the wrong side, the charges would not balance.) By observing the locations of the electrons in the equations (on the right for oxidation; on the left for reduction), we come to the same conclusions that Mg is oxidized and O_2 is reduced.

Another check is noting that we've identified one substance as being oxidized and the other as being reduced. If we had made a mistake, we might have concluded that both were oxidized, or both were reduced. But that's impossible, because in every reaction in which there is oxidation, there must also be reduction.

Practice Exercises

6.1 | When sodium reacts with molecular oxygen, O_2, the product is sodium peroxide, Na_2O_2, which contains the peroxide ion, O_2^{2-}. In this reaction, is O_2 oxidized or reduced? (*Hint:* Which reactant gains electrons, and which loses electrons?)

6.2 | Identify the substances oxidized and reduced, and the oxidizing and reducing agents in the reaction of aluminum and chlorine to form aluminum chloride.

6.3 | On page 134 we described the thermite reaction in which iron(III) oxide reacts with aluminum to form metallic iron and aluminum oxide. Identify the substances oxidized and reduced and the oxidizing and reducing agents in this reaction.

Using Oxidation Numbers to Follow Redox Changes

Unlike the reaction of magnesium with oxygen, not all reactions with oxygen produce ionic products. For example, sulfur reacts with oxygen to give sulfur dioxide, SO_2, which is molecular. Nevertheless, it is convenient to also view this as a redox reaction, but this requires that we change the way we define oxidation and reduction. To do this, chemists developed a bookkeeping system called **oxidation numbers,** which provides a way to keep tabs on electron transfers.

The oxidation number of an element in a particular compound is assigned according to a set of rules, which are described below. For simple, monatomic ions in a compound such as NaCl, the oxidation numbers are the same as the charges on the ions, so in NaCl the oxidation number of Na^+ is $+1$ and the oxidation number of Cl^- is -1. The real value of oxidation numbers is that they can also be assigned to atoms in molecular compounds. In such cases, it is important to realize that the oxidation number does not actually equal a charge on an atom. To be sure to differentiate oxidation numbers from actual electrical charges, we will specify the sign *before* the number when writing oxidation numbers, and *after* the number when writing electrical charges. Thus, a sodium ion has a charge of 1+ and an oxidation number of $+1$.

A term that is frequently used interchangeably with *oxidation number* is **oxidation state.** In NaCl, sodium has an oxidation number of $+1$ and is said to be "in the $+1$ oxidation state." Similarly, the chlorine in NaCl is said to be in the -1 oxidation state. When there are more than one possible oxidation states, the oxidation state of an element is given by writing the oxidation number as a Roman numeral in parentheses after the name of the element. For example, "iron(III)" means iron in the $+3$ oxidation state. A summary of the terms used in oxidation and reduction reactions is given in Table 6.1.

We can use these new terms now to redefine a redox reaction.

> A **redox reaction** is a chemical reaction in which changes in oxidation numbers occur.

Table 6.1 **Summary of Oxidation and Reduction Using $2Na + Cl_2 \longrightarrow 2NaCl$**

Sodium	Chlorine
Oxidized	Reduced
Reducing agent	Oxidizing agent
Oxidation number increases	Oxidation number decreases
Loses electrons	Gains electrons

We can follow redox reactions by taking note of the changes in oxidation numbers. To do this, however, we must be able to assign oxidation numbers to atoms in a quick and simple way.

Rules for the Assignment of Oxidation Numbers

We can use some basic knowledge learned earlier plus the set of rules below to determine the oxidation numbers of the atoms in almost any compound. These rules are a hierarchy; use the lower numbered rule first, and then apply the higher numbered rule. This allows us to deal with conflicts between two rules.

A Hierarchy of Rules for Assigning Oxidation Numbers

1. Oxidation numbers must add up to the charge on the molecule, formula unit, or ion.
2. The atoms of free elements have oxidation numbers of zero.
3. Metals in Groups 1A, 2A, and Al have +1, +2, and +3 oxidation numbers, respectively.
4. H and F in compounds have +1 and −1 oxidation numbers, respectively.
5. Oxygen has a −2 oxidation number.
6. Group 7A elements have a −1 oxidation number.
7. Group 6A elements have a −2 oxidation number.
8. Group 5A elements have a −3 oxidation number.
9. When there is a conflict between two of these rules or an ambiguity in assigning an oxidation number, apply the rule with the lower number and ignore the conflicting rule.

TOOLS

Assigning oxidation numbers

- Rule 2 means that O in O_2, P in P_4, and S in S_8 all have oxidation numbers of zero.
- For example, hydrogen can have an oxidation number of −1 when combined with a metal in Group 1A. If we follow Rules 1 and 3 first, then we can ignore Rule 4 and give H the −1 oxidation number.

These rules can be applied to elements, molecules, and ionic compounds. For example, oxygen, O_2, is a free element and has a zero charge, the oxidation number for each oxygen atom in O_2 must be zero, following Rules 1 and 2. Or, take the simple ionic compound, NaCl: the sodium is in Group 1A and has an oxidation number of +1, from Rule 3; and from Rule 6, chlorine has an oxidation number of −1. These add up to zero, which is the overall charge of the formula unit.

The numbered rules and their order in the list given above come into play when an element is capable of having more than one oxidation state. For example, you learned that transition metals can form more than one ion. Iron, for example, forms Fe^{2+} and Fe^{3+} ions, so in an iron compound we have to use the rules to figure out which iron ion is present. Similarly, when nonmetals are combined with hydrogen and oxygen in compounds or polyatomic ions, their oxidation numbers can vary and must be calculated using the rules. For example, one of the products of the oxidation of isoprene is formaldehyde, CH_2O. The oxidation of the carbon atom can be calculated using the numbered rules. The two hydrogens together are $2 \times (+1)$ and the oxygen has an oxidation number of −2. Together they add up to zero, and since the molecule is neutral, the carbon must have an oxidation number of 0, according to Rule 1.

With this as background, let's look at some more examples that illustrate how we apply the rules.

Example 6.2
Assigning Oxidation Numbers

Titanium dioxide, TiO_2, is a white pigment used in making paint. A now outmoded process of making TiO_2 from its ore involved $Ti(SO_4)_2$ as an intermediate. What is the oxidation number of titanium in $Ti(SO_4)_2$?

Analysis: The key here is recognizing SO_4 as the sulfate ion, SO_4^{2-}. Because we're only interested in the oxidation number of titanium, we use the charge on SO_4^{2-} to equal the net oxidation number of the polyatomic ion.

Assembling the Tools: We will use the rules for assigning oxidation numbers and most important, Rule 1, to sum the oxidation numbers to equal the overall charge of the formula unit. The charge on a polyatomic ion is the *net* oxidation number of the ion.

Solution: The sulfate ion has a charge of 2−, which we can take to be its net oxidation number. Then, we apply the summation rule (Rule 1) to find the oxidation number of titanium, which we will represent by x.

$$\begin{array}{llrl} \text{Ti} & (1\text{ atom}) \times (x) = & x & \\ SO_4^{2-} & (2\text{ ions}) \times (-2) = & -4 & \\ \hline & \text{Sum} = & 0 & \quad (\text{Rule 1}) \end{array}$$

Obviously, the oxidation number of titanium is +4 so that the sum can be zero.

Is the Answer Reasonable? We have the sum of oxidation numbers adding up to zero, the charge on $Ti(SO_4)_2$, so our answer is reasonable.

As we have already discussed, transition metals can have more than one oxidation state. In addition, the oxidation states of the nonmetals can vary depending on the compound they are in. For example, sulfur can be found in H_2S, S (elemental sulfur), SO_2, SO_3, and H_2SO_4. The oxidation states for sulfur are −2, 0, +4, +6, and +6, respectively. Example 6.3 illustrates this same point with oxygen.

Example 6.3
Assigning Oxidation Numbers

diamond
Solution of hydrogen peroxide
U.S.P. 10 Volume 3%
16 FL. OZ. (1 PINT)

Hydrogen peroxide destroys bacteria by oxidizing them. *(Robert Capece)*

Determine the oxidation numbers of the atoms in hydrogen peroxide, H_2O_2, a common antiseptic purchased in pharmacies, which can also be used to bleach hair.

Analysis: The compound is molecular, so there are no ions to work with; we have to find the oxidation numbers for the hydrogen and the oxygen.

Assembling the Tools: Just as in Example 6.2, we will use the tool for assigning oxidation numbers, and apply the appropriate rules. We can start by scanning the rules, and we see we have one for hydrogen and another for oxygen. We always have to keep in mind Rule 1, adding up the oxidation numbers, and Rule 9, how to handle conflicts between rules.

Solution: Let us start with hydrogen and Rule 4, which tells us to assign an oxidation number of +1 to hydrogen. Rule 5 tells us to give oxygen an oxidation number of −2. Both of these can't be correct, because the sum must be zero (Rule 1).

$$\begin{array}{llrl} \text{H} & (2\text{ atoms}) \times (+1) = & +2 & \quad (\text{Rule 4}) \\ \text{O} & (2\text{ atoms}) \times (-2) = & -4 & \quad (\text{Rule 5}) \\ \hline & \text{Sum} \neq & 0 & \quad (\text{violates Rule 1}) \end{array}$$

As mentioned above, when there is a conflict between the rules, we ignore the higher numbered rule that causes the conflict.

Rule 5 is the higher numbered rule causing the conflict, so we have to ignore it and just apply Rules 1 (the sum rule) and 4 (the rule that tells us the oxidation number of hydrogen is $+1$). Because we don't have a rule that applies to oxygen in this case, we'll represent the oxidation number of O by x.

$$\begin{array}{lr}\text{H} \quad (2 \text{ atoms}) \times (+1) = +2 & \text{(Rule 4)} \\ \text{O} \quad (2 \text{ atoms}) \times (x) = 2x & \\ \hline \text{Sum} = 0 & \text{(Rule 1)}\end{array}$$

For the sum to be zero, $2x = -2$, so $x = -1$. Therefore, in this compound, oxygen has an oxidation number of -1.

$$\text{H} = +1 \qquad \text{O} = -1$$

Is the Answer Reasonable? A conflict between the rules occurs only rarely, but when it happens the conflict becomes apparent because it causes a violation of the sum rule. However, *the sum rule (Rule 1) always applies.*

Sometimes, oxidation numbers calculated by the rules have fractional values, as illustrated in Example 6.4.

Example 6.4
Assigning Oxidation Numbers

The air bags used as safety devices in modern autos are inflated by the very rapid decomposition of the ionic compound sodium azide, NaN_3. The reaction gives elemental sodium and gaseous nitrogen. What is the average oxidation number of the nitrogen in sodium azide?

The explosive decomposition of sodium azide releases nitrogen gas, which rapidly inflates an air bag during a crash. *(Corbis-Bettmann)*

Analysis: We're told that NaN_3 is ionic, so we know that there is a cation and an anion. The cation is the sodium ion, Na^+, which means that the remainder of the formula unit, "N_3" must carry one unit of negative charge. However, there could not be three nitrogen anions each with a charge of $\frac{1}{3}-$, because it would mean that each nitrogen atom had acquired one-third of an electron. Whole numbers of electrons are always involved in electron transfers. Therefore, the anion must be a single particle with a negative one charge, namely, N_3^-. For this anion, the sum of the oxidation numbers of the three nitrogen atoms must be -1. We can use this information to solve the problem.

Assembling the Tools: We will use the same tools as in Example 6.3—namely, the assignment of oxidation numbers, and we will focus on Rules 1 and 3.

Solution: The sum of the oxidation numbers of the nitrogen must be equal to -1. If we let x stand for the oxidation number of just one of the nitrogen atoms, then

$$(3 \text{ atoms}) \times (x) = 3x = -1$$

$$x = -\tfrac{1}{3}$$

We could have also tackled the problem just using the rules for assigning oxidation numbers. We know that sodium exists as the ion Na^+ and that the compound is neutral overall. Therefore,

$$\begin{array}{lr}\text{Na} \quad (1 \text{ atom}) \times (+1) = +1 & \text{(Rule 3)} \\ \text{N} \quad (3 \text{ atoms}) \times (x) = 3x & \\ \hline \text{Sum} = 0 & \text{(Rule 1)}\end{array}$$

The sum of the oxidation numbers of the three nitrogen atoms in this ion must add up to -1, so each nitrogen must have an oxidation number of $-\frac{1}{3}$.

Is the Answer Reasonable? As with Example 6.3, we've solved it two ways, so we can certainly feel confident the answer is correct.

Practice Exercises

6.4 | The chlorite ion, ClO_2^-, is a potent disinfectant, and solutions of it are sometimes used to disinfect air-conditioning systems in cars. What is the oxidation number of chlorine in this ion? (*Hint:* The sum of the oxidation numbers is not zero.)

6.5 | Assign oxidation numbers to each atom in (a) $NiCl_2$, (b) Mg_2TiO_4, (c) $K_2Cr_2O_7$, (d) HPO_4^{2-}, (e) $V(C_2H_3O_2)_3$, and (f) NH_4^+.

6.6 | Iron forms a magnetic oxide with the formula Fe_3O_4 that contains both Fe^{2+} and Fe^{3+} ions. What is the *average* oxidation number of iron in this oxide?

6.7 | Molybdenum can form compounds with many different oxidation numbers. Assign the oxidation numbers for molybdenum in (a) $MoCl_3$, (b) MoS_2, (c) $MoOCl_4$, and (d) MoP_2.

Identifying Oxidation and Reduction Processes

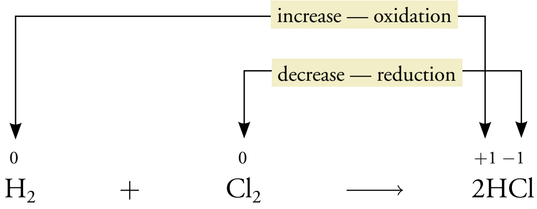
Oxidation numbers can be used in several ways. One is to define oxidation and reduction in the most comprehensive manner, as follows:

TOOLS

Oxidation and reduction reactions

> **Oxidation** involves an increase in oxidation number.
>
> **Reduction** involves a decrease in oxidation number.

Let's see how these definitions apply to the reaction of hydrogen with chlorine. To avoid confusing oxidation numbers with actual electrical charges, we will write oxidation numbers directly above the chemical symbols of the elements.



$$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow 2\overset{+1}{H}\overset{-1}{Cl}$$

Notice that we have assigned the atoms in H_2 and Cl_2 oxidation numbers of zero, since they are free elements. The changes in oxidation number tell us that hydrogen is oxidized and chlorine is reduced.

Example 6.5
Using Oxidation Numbers to Follow Redox Reactions

Is the following a redox reaction?

$$2KCl + MnO_2 + 2H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$$

If so, identify the substance oxidized and the substance reduced, as well as the oxidizing and reducing agents.

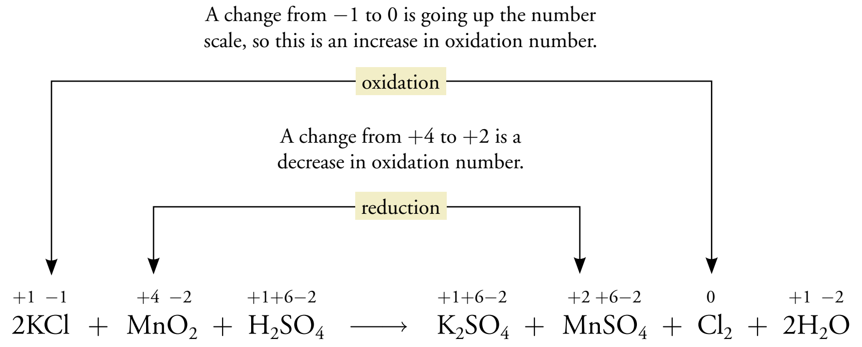
Analysis: To determine whether the reaction is redox and to give the specific answers requested, we will need to determine whether oxidation numbers are changing and how they are changing in the reaction.

Assembling the Tools: Our tools will be the rules for assigning oxidation numbers and the revised definitions of oxidation and reduction. Applying the tool to each element will tell us whether redox is occurring, and if so, what is oxidized and what is reduced. Then, applying the tool for the definition of oxidizing and reducing agents, we recall that the substance oxidized is the reducing agent, and the substance reduced is the oxidizing agent.

Solution: To determine whether redox is occurring here, we first assign oxidation numbers to each atom on both sides of the equation. Following the rules, we get

$$\overset{+1\ -1}{2KCl} + \overset{+4\ -2}{MnO_2} + \overset{+1+6-2}{H_2SO_4} \longrightarrow \overset{+1+6-2}{K_2SO_4} + \overset{+2\ +6-2}{MnSO_4} + \overset{0}{Cl_2} + \overset{+1\ -2}{2H_2O}$$

Next, we look for changes, keeping in mind that an increase in oxidation number is oxidation and a decrease is reduction.


A change from −1 to 0 is going up the number scale, so this is an increase in oxidation number.

A change from +4 to +2 is a decrease in oxidation number.

$$\overset{+1\ -1}{2KCl} + \overset{+4\ -2}{MnO_2} + \overset{+1+6-2}{H_2SO_4} \longrightarrow \overset{+1+6-2}{K_2SO_4} + \overset{+2\ +6-2}{MnSO_4} + \overset{0}{Cl_2} + \overset{+1\ -2}{2H_2O}$$

Thus, the Cl in KCl is oxidized and the Mn in MnO_2 is reduced. The reducing agent is KCl and the oxidizing agent is MnO_2. (Notice that when we identify the oxidizing and reducing agents, we give the entire formulas for the substances that contain the atoms with oxidation numbers that change.)

Is the Answer Reasonable? There are lots of things we could check here. We have found changes that lead us to conclude that redox is happening. We can also identify one change as oxidation and the other as reduction, which gives us confidence that we've done the rest of the work correctly.

Practice Exercises

6.8 | Consider the following reactions:

$$N_2O_5 + 2NaHCO_3 \longrightarrow 2NaNO_3 + 2CO_2 + H_2O$$
$$KClO_3 + 3HNO_2 \longrightarrow KCl + 3HNO_3$$

Which one is a redox reaction? For the redox reaction, which compound is oxidized and which is reduced? (*Hint:* How is redox defined using oxidation numbers?)

6.9 | Chlorine dioxide, ClO_2, is used to kill bacteria in the dairy industry, meat industry, and other food and beverage industry applications. It is unstable, but can be made by the following reaction:

$$Cl_2 + 2NaClO_2 \longrightarrow 2ClO_2 + 2NaCl$$

Identify the substances oxidized and reduced, as well as the oxidizing and reducing agents in the reaction.

6.10 | When hydrogen peroxide is used as an antiseptic, it kills bacteria by oxidizing them. When the H_2O_2 serves as an oxidizing agent, which product might be formed from it, O_2 or H_2O? Why?

6.11 | Burning methane in oxygen gives carbon dioxide and water according to the following reaction:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

What species is being oxidized and what species is being reduced? Identify the reducing agent and the oxidizing agent.

6.2 | Balancing Redox Equations

Many redox reactions take place in aqueous solution and many of these involve ions. An example is the reaction of laundry bleach with substances in the wash water. The active ingredient in the bleach is hypochlorite ion, OCl^-, which is the oxidizing agent in these reactions. To study redox reactions, it is often helpful to write the ionic and net ionic equations, just as we did in our analysis of metathesis reactions earlier in Chapter 5. In addition, one of the easiest ways to balance equations for redox reactions is to follow a procedure called the ion–electron method.

The Ion–Electron Method: A Divide and Conquer Approach

In the **ion–electron method**, we divide the oxidation and reduction processes into individual equations called **half-reactions** that are balanced separately. Each half-reaction is made to obey *both* criteria for a balanced ionic equation: *both atoms and charge have to balance.* Then, we combine the balanced half-reactions to obtain the fully balanced net ionic equation.

In balancing the half-reactions, we must take into account that for many redox reactions in aqueous solutions, H^+ or OH^- ions play an important role, as do water molecules. For example, when solutions of $K_2Cr_2O_7$ and $FeSO_4$ are mixed, the acidity of the mixture decreases as dichromate ion, $Cr_2O_7^{2-}$, oxidizes Fe^{2+} (Figure 6.2). This is because the reaction uses up H^+ as a reactant and produces H_2O as a product. In other reactions, OH^- is consumed, while in still others, H_2O is a reactant. Another fact is that in many cases the products (or even the reactants) of a redox reaction will differ depending on the acidity of the solution. For example, in an acidic solution, MnO_4^- is reduced to the Mn^{2+} ion, but in a neutral or slightly basic solution, the reduction product is insoluble the MnO_2.

■ Equations for redox reactions are often more complex than those for metathesis reactions and can be difficult to balance by inspection. The ion–electron method provides a systematic procedure for balancing redox equations.

■ For simplicity, we are using H^+ to stand for H_3O^+ throughout our discussions in this chapter.

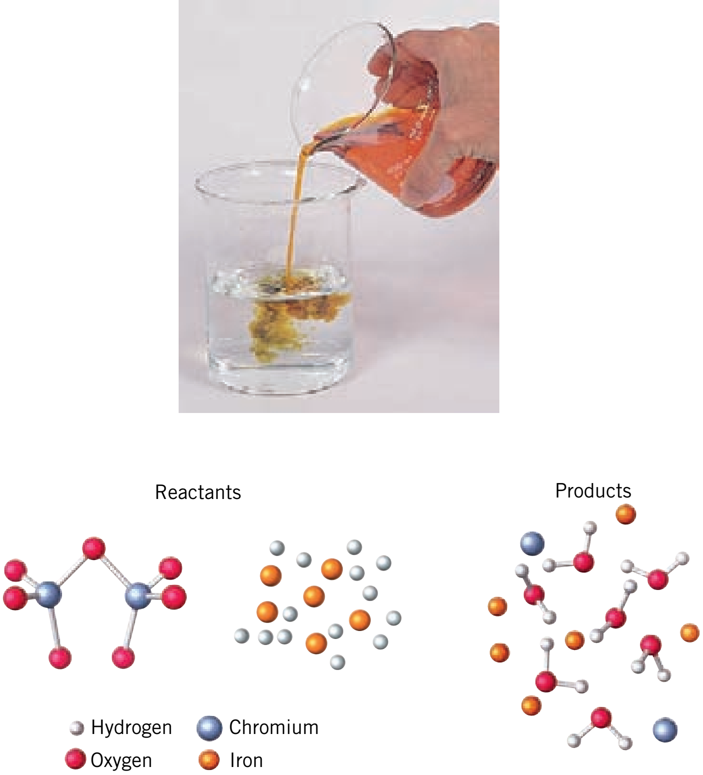


Figure 6.2 | **A redox reaction taking place in an acidic solution.** A solution of $K_2Cr_2O_7$ oxidizes Fe^{2+} to Fe^{3+} in an acidic solution, while the orange dichromate ion is reduced to Cr^{3+}. *(Peter Lerman)*

Because of these factors, redox reactions are generally carried out in solutions containing a substantial excess of either acid or base, so before we can apply the ion–electron method, we have to know whether the reaction occurs in an acidic or a basic solution. (This information will always be given to you in this book.)

Balancing Redox Equations in Acidic Solutions

As you just learned, $Cr_2O_7^{2-}$ reacts with Fe^{2+} in an acidic solution to give Cr^{3+} and Fe^{3+} as products. This information permits us to write the **skeleton equation**, which shows only the ions (or molecules) involved in the redox changes. We will leave out the spectator ions, K^+ and SO_4^{2-}, since they do not react in this redox reaction.

$$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$$

We then proceed through the steps described below to find the balanced equation. As you will see, the ion–electron method will tell us how H^+ and H_2O are involved in the reaction; we don't need to know this in advance.

Step 1. ***Divide the skeleton equation into half-reactions.*** We choose one of the reactants, $Cr_2O_7^{2-}$, and write it at the left of an arrow. On the right, we write what $Cr_2O_7^{2-}$ changes to, which is Cr^{3+}. This gives us the beginnings of one half-reaction. For the second half-reaction, we write the other reactant, Fe^{2+}, on the left and the other product, Fe^{3+}, on the right. *Notice that we are careful to use the complete formulas for the ions that appear in the skeleton equation.* Except for hydrogen and oxygen, the same elements must appear on both sides of a given half-reaction.

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$
$$Fe^{2+} \longrightarrow Fe^{3+}$$

■ Many students tend to forget this step. If you do, you may end up in trouble later on.

Step 2. ***Balance atoms other than H and O.*** There are two Cr atoms on the left and only one on the right, so we place a coefficient of 2 in front of Cr^{3+}. The second half-reaction is already balanced in terms of atoms, so we leave it as is.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$
$$Fe^{2+} \longrightarrow Fe^{3+}$$

■ We use H_2O, not O or O_2, to balance oxygen atoms, because H_2O is what is actually reacting or being produced in the solution.

Step 3. ***Balance oxygen by adding H_2O to the side that needs O.*** There are seven oxygen atoms on the left of the first half-reaction and none on the right. Therefore, we add $7H_2O$ to the right side of the first half-reaction to balance the oxygens. (There is no oxygen imbalance in the second half-reaction, so there's nothing to do there.)

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+}$$

The oxygen atoms now balance, but we've created an imbalance in hydrogen. We address that issue next.

Step 4. ***Balance hydrogen by adding H^+ to the side that needs H.*** After adding the water, we see that the first half-reaction has 14 hydrogens on the right and none on the left. To balance hydrogen, we add $14H^+$ to the left side of the half-reaction. When you do this step (or others) *be careful to write the charges on the ions.* If they are omitted, you will not obtain a balanced equation in the end.

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+}$$

Now each half-reaction is balanced in terms of atoms. Next, we will balance the charge.

Step 5. ***Balance the charge by adding electrons.*** First, we compute the net electrical charge on each side. For the first half-reaction we have

$$\underbrace{14H^+ + Cr_2O_7^{2-}}_{\text{Net charge} = (14+) + (2-) = 12+} \longrightarrow \underbrace{2Cr^{3+} + 7H_2O}_{\text{Net charge} = 2(3+) + 0 = 6+}$$

The algebraic difference between the net charges on the two sides equals the number of electrons that must be added to the more positive (or less negative) side. In this instance, we must add $6e^-$ to the left side of the half-reaction.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

This half-reaction is now complete; it is balanced in terms of both atoms and charge. (We can check this by recalculating the charge on both sides.)

To balance the other half-reaction, we add one electron to the right.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Now this reaction is balanced for both mass and charge.

Step 6. ***Make the number of electrons gained equal to the number lost and then add the two half-reactions.*** At this point we have the two balanced half-reactions

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Six electrons are gained in the first, but only one is lost in the second. Therefore, before combining the two equations we multiply all of the coefficients of the second half-reaction by 6.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$$

$$\text{(Sum) } 6e^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^-$$

■ Because we know the electrons will cancel, we really don't have to carry them down into the combined equation. We've done so here just for emphasis.

Step 7. ***Cancel anything that is the same on both sides.*** This is the final step. Six electrons cancel from both sides to give the final balanced equation.

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

Notice that both the charge and the atoms balance.

In some reactions, after adding the two half-reactions you may have H_2O or H^+ on both sides—for example, $6H_2O$ on the left and $2H_2O$ on the right. Cancel as many as you can. Thus,

$$\ldots + 6H_2O \ldots \longrightarrow \ldots + 2H_2O \ldots$$

reduces to

$$\ldots + 4H_2O \ldots \longrightarrow \ldots$$

The following is a summary of the steps we've followed for balancing an equation for a redox reaction in an acidic solution. If you don't skip any steps and you perform them in the order given, you will always obtain a properly balanced equation.

TOOLS

Ion–electron method for acidic solutions

Ion–Electron Method—Acidic Solution

Step 1. Divide the equation into two half-reactions.
Step 2. Balance atoms other than H and O.
Step 3. Balance O by adding H_2O.
Step 4. Balance H by adding H^+.
Step 5. Balance net charge by adding e^-.
Step 6. Make e^- gain equal e^- loss; then add half-reactions.
Step 7. Cancel anything that's the same on both sides.

■ At both Steps 5 and 7, check that the equations are balanced for both mass and charge.

Example 6.6
Using the Ion–Electron Method

Balance the following equation:

$$MnO_4^- + H_2SO_3 \longrightarrow SO_4^{2-} + Mn^{2+}$$

The reaction occurs in an acidic solution.

■ **Analysis:** In using the ion–electron method, there's not much to analyze. It's necessary to know the steps and to follow them in sequence.

■ **Assembling the Tools:** Follow the seven steps of the ion–electron method for acidic solutions to balance the equation.

■ **Solution:** We follow the steps given above.

Step 1. Divide the skeleton equation into two half-reactions.

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$H_2SO_3 \longrightarrow SO_4^{2-}$$

Step 2. Balance atoms other than H and O. There is nothing to do for this step. All the atoms except H and O are already in balance.

Step 3. Add H_2O to balance oxygens.

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$H_2O + H_2SO_3 \longrightarrow SO_4^{2-}$$

Step 4. Add H^+ to balance H.

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$H_2O + H_2SO_3 \longrightarrow SO_4^{2-} + 4H^+$$

Step 5. Balance the charge by adding electrons to the more positive side.

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$H_2O + H_2SO_3 \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Step 6. Make electron loss equal to electron gain, then add the half-reactions.

$$2(5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O)$$

$$5(H_2O + H_2SO_3 \longrightarrow SO_4^{2-} + 4H^+ + 2e^-)$$

$$10e^- + 16H^+ + 2MnO_4^- + 5H_2O + 5H_2SO_3 \longrightarrow 2Mn^{2+} + 8H_2O + 5SO_4^{2-} + 20H^+ + 10e^-$$

Step 7. Cancel $10e^-$, $16H^+$, and $5H_2O$ from both sides. The final equation is

$$2MnO_4^- + 5H_2SO_3 \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + 4H^+$$

■ **Is the Answer Reasonable?** The check involves *two* steps. First, we check that each side of the equation has the same number of atoms of each element, which it does. Second, we check to be sure that the net charge is the same on both sides. On the left we have $2MnO_4^-$ with a net charge of 2−. On the right we have $2Mn^{2+}$ and $4H^+$ (total charge = 8+) along with $5SO_4^{2-}$ (total charge = 10−), so the net charge is also 2−. Having both atoms *and* charge in balance makes it a balanced equation and confirms that we've worked the problem correctly.

Practice Exercises

6.12 | Explain why the following equation is not balanced. Balance it using the ion–electron method. (*Hint:* What are the criteria for a balanced ionic equation?)

$$\mathrm{Al} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Al}^{3+} + \mathrm{Cu}$$

6.13 | The element technetium (atomic number 43) is radioactive and one of its isotopes, $^{99}\mathrm{Tc}$, is used in medicine for diagnostic imaging. The isotope is usually obtained in the form of the pertechnetate anion, $\mathrm{TcO_4}^-$, but its use sometimes requires the technetium to be in a lower oxidation state. Reduction can be carried out using Sn^{2+} in an acidic solution. The skeleton equation is

$$\mathrm{TcO_4}^- + \mathrm{Sn}^{2+} \longrightarrow \mathrm{Tc}^{4+} + \mathrm{Sn}^{4+} \qquad \text{(acidic solution)}$$

Balance the equation by the ion–electron method.

6.14 | What is the balanced net ionic equation for the following reaction in an acidic solution?

$$\mathrm{Cu} + \mathrm{NO_3}^- \longrightarrow \mathrm{Cu}^{2+} + \mathrm{N_2O}$$

6.15 | When pyridine (C_5H_5N), a compound used in the manufacturing of drugs and vitamins, is burned, carbon dioxide, nitrogen dioxide, and water are formed. Balance the following equation by the ion–electron method.

$$\mathrm{C_5H_5N} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{NO_2} + \mathrm{H_2O}$$

Balancing Redox Equations for Basic Solutions

In a basic solution, the concentration of H^+ is very small; the dominant species are H_2O and OH^-. Strictly speaking, these should be used to balance the half-reactions. However, the simplest way to obtain a balanced equation for a basic solution is to first *pretend* that the solution is acidic. We balance the equation using the seven steps just described, and then we use a simple three-step procedure described below to convert the equation to the correct form for a basic solution. The conversion uses the fact that H^+ and OH^- react in a 1-to-1 ratio to give H_2O.

TOOLS

Ion–electron method for basic solutions

Additional Steps in the Ion–Electron Method for Basic Solutions

Step 8. Add to *both* sides of the equation the same number of OH^- as there are H^+.
Step 9. Combine H^+ and OH^- to form H_2O.
Step 10. Cancel any H_2O that you can.

■ Again, checking that the equation is balanced for both mass and charge is essential at the end of this process.

As an example, suppose we wanted to balance the following equation for a basic solution.

$$\mathrm{SO_3}^{2-} + \mathrm{MnO_4}^- \longrightarrow \mathrm{SO_4}^{2-} + \mathrm{MnO_2}$$

Following Steps 1 through 7 for acidic solutions gives

$$2\mathrm{H}^+ + 3\mathrm{SO_3}^{2-} + 2\mathrm{MnO_4}^- \longrightarrow 3\mathrm{SO_4}^{2-} + 2\mathrm{MnO_2} + \mathrm{H_2O}$$

Conversion of this equation to one appropriate for a basic solution proceeds as follows.

Step 8. ***Add to both sides of the equation the same number of OH^- as there are H^+.*** The equation for acidic solution has $2H^+$ on the left, so we add $2OH^-$ to *each* side. This gives

$$2\mathrm{OH}^- + 2\mathrm{H}^+ + 3\mathrm{SO_3}^{2-} + 2\mathrm{MnO_4}^- \longrightarrow 3\mathrm{SO_4}^{2-} + 2\mathrm{MnO_2} + \mathrm{H_2O} + 2\mathrm{OH}^-$$

Step 9. ***Combine H^+ and OH^- to form H_2O.*** The left side has $2OH^-$ and $2H^+$, which become $2H_2O$. So in place of $2OH^- + 2H^+$ we write $2H_2O$.

$$\underbrace{2OH^- + 2H^+}_{\big\downarrow} + 3SO_3^{2-} + 2MnO_4^- \longrightarrow 3SO_4^{2-} + 2MnO_2 + H_2O + 2OH^-$$

$$2H_2O + 3SO_3^{2-} + 2MnO_4^- \longrightarrow 3SO_4^{2-} + 2MnO_2 + H_2O + 2OH^-$$

Step 10. ***Cancel any H_2O that you can.*** In this equation, one H_2O can be eliminated from both sides. The final equation, balanced for basic solution, is

$$H_2O + 3SO_3^{2-} + 2MnO_4^- \longrightarrow 3SO_4^{2-} + 2MnO_2 + 2OH^-$$

Practice Exercises

6.16 | Consider the following half-reaction balanced for an acidic solution:

$$2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

What is the balanced half-reaction for a basic solution? (*Hint:* Remember that H^+ and OH^- react to form H_2O.)

6.17 | Balance the following equation for a basic solution.

$$MnO_4^- + C_2O_4^{2-} \longrightarrow MnO_2 + CO_3^{2-}$$

6.18 | The reaction of Br_2 with itself can be carried out in basic solutions.

$$Br_2 \longrightarrow BrO_3^- + Br^-$$

Balance the equation in a basic solution.

6.19 | Alkaline batteries last longer than if the reaction were carried out under acidic conditions. The reaction for alkaline batteries is

$$Zn + MnO_2 \longrightarrow ZnO + Mn_2O_3$$

Balance the equation in a basic solution.

6.3 | Acids as Oxidizing Agents

Earlier you learned that one of the properties of acids is that they react with bases. Another important property is their ability to react with certain metals. These are redox reactions in which the metal is oxidized and the acid is reduced. However, in these reactions, the part of the acid that's reduced depends on the composition of the acid itself as well as on the metal.

When a piece of zinc is placed into a solution of hydrochloric acid, bubbling is observed and the zinc gradually dissolves (Figure 6.3). The chemical reaction is

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

for which the net ionic equation is

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

In this reaction, zinc is oxidized and hydrogen ions are reduced. Stated another way, *the H^+ of the acid is the oxidizing agent.*

Many metals react with acids just as zinc does—by being oxidized by hydrogen ions. In these reactions a metal salt and gaseous hydrogen are the products.

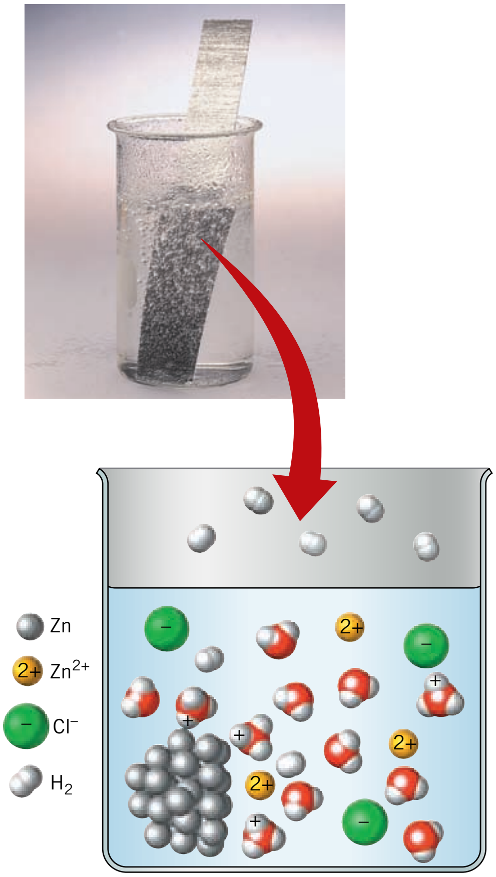


Figure 6.3 | **Zinc reacts with hydrochloric acid.** Bubbles of hydrogen are formed when a solution of hydrochloric acid comes in contact with metallic zinc. The same reaction takes place if hydrochloric acid is spilled on galvanized (zinc-coated) steel. In the molecular view (not balanced), the hydronium ions react with the zinc metal atoms (dark gray spheres). Two hydrogen ions gain two electrons from the metal atom and form a hydrogen molecule, and the zinc is oxidized to a cation with a 2+ charge. *(Richard Megna/ Fundamental Photographs)*

Metals that are able to react with acids such as HCl and H_2SO_4 to give hydrogen gas are said to be *more active* than hydrogen (H_2). For other metals, however, hydrogen ions are not powerful enough to cause their oxidation. Copper, for example, is significantly less reactive than zinc or iron, and H^+ cannot oxidize it. Copper is an example of a metal that is *less active* than H_2.

The Anion Determines the Oxidizing Power of an Acid

Hydrochloric acid contains H_3O^+ ions (which is sometimes abbreviated as H^+) and Cl^- ions. The hydronium ion in hydrochloric acid can be an oxidizing agent because it can be reduced to H_2. However, the Cl^- ion in the solution has no tendency at all to be an oxidizing agent, so in a solution of HCl the only oxidizing agent is H_3O^+. The same applies to dilute solutions of sulfuric acid, H_2SO_4.

■ The strongest oxidizing agent in a solution of a "nonoxidizing" acid is H^+.

The hydrogen ion in water is actually a rather poor oxidizing agent, so hydrochloric acid and sulfuric acid have rather poor oxidizing abilities. They are often called **nonoxidizing acids,** even though their hydronium ions are able to oxidize certain metals. Therefore, in a nonoxidizing acid, the *anion* of the acid is a weaker oxidizing agent than H_3O^+ and the anion of the acid is more difficult to reduce than H_3O^+. Some acids contain anions that are stronger oxidizing agents than H_3O^+ and are called **oxidizing acids.** (See Table 6.2.)

Nitrate Ion as an Oxidizing Agent

Nitric acid, HNO_3, ionizes in water to give H^+ and NO_3^- ions. In this solution, the nitrate ion is a more powerful oxidizing agent than the hydrogen ion. This makes it able to oxidize metals that H^+ cannot, such as copper and silver. For example, the molecular equation for the reaction of concentrated HNO_3 with copper, shown in Figure 6.4, is

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O$$

Table 6.2 **Nonoxidizing and Oxidizing Acids**

Nonoxidizing Acids
HCl(*aq*)
$H_2SO_4(aq)$[a]
$H_3PO_4(aq)$
Most organic acids (e.g., $HC_2H_3O_2$)

Oxidizing Acids	**Conditions**	**Reduction Reaction**
HNO_3	Concentrated	$NO_3^- + 2H^+ + e^- \longrightarrow NO_2(g) + H_2O$
	Dilute	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$
	Very dilute, with strong reducing agent	$NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O$
H_2SO_4	Hot, concentrated, with strong reducing agent	$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S(g) + 4H_2O$
	Hot, concentrated	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow SO_2(g) + 2H_2O$

[a] H_2SO_4 is a nonoxidizing acid when cold and dilute.

Oxidizing and nonoxidizing acids

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

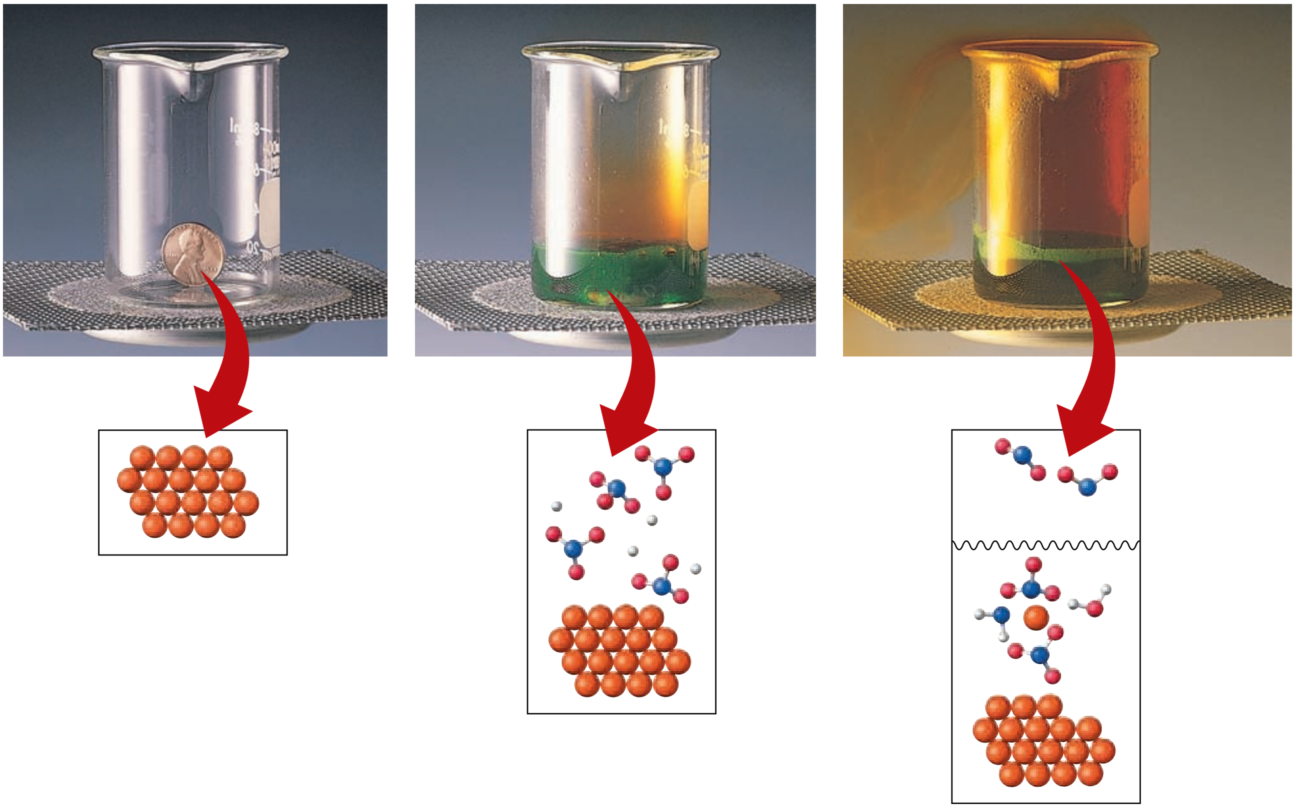
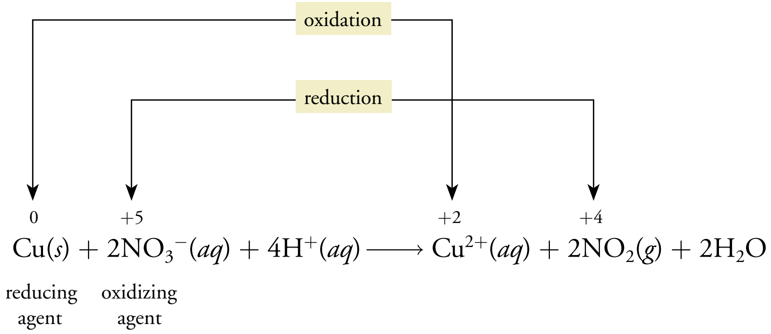


Figure 6.4 | **The reaction of copper with concentrated nitric acid.** A copper penny reacts vigorously with concentrated nitric acid, as this sequence of photographs shows. The dark red-brown vapors are nitrogen dioxide, the same gas that gives smog its characteristic color. The atomic view shows the copper in the solid, the addition of nitric acid, and finally, the formation of the copper nitrate, nitrogen dioxide as a gas, and water molecules. *(Michael Watson)*

If we convert this to a net ionic equation and then assign oxidation numbers, we can see that NO_3^- is the oxidizing agent and Cu is the reducing agent.



$$\overset{0}{Cu}(s) + 2\overset{+5}{N}O_3^-(aq) + 4H^+(aq) \longrightarrow \overset{+2}{Cu}{}^{2+}(aq) + 2\overset{+4}{N}O_2(g) + 2H_2O$$

Notice that in this reaction, *no hydrogen gas is formed*. The H^+ ions of the HNO_3 are an essential part of the reaction, but they just become part of water molecules without a change in oxidation number.

The nitrogen-containing product formed in the reduction of nitric acid depends on the concentration of the acid and the reducing power of the metal. With *concentrated* nitric acid, nitrogen dioxide, NO_2, is often the reduction product. With *dilute* nitric acid, the product is often nitrogen monoxide (also called nitric oxide), NO, instead. Copper, for example, reacts as follows:

Concentrated HNO_3

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O$$

Dilute HNO_3

$$3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O$$

■ Nitric acid causes severe skin burns, so be careful when you work with it in the laboratory. If you spill any on your skin, wash it off immediately and seek the help of your lab teacher.

Nitric acid is a very effective oxidizing acid. All metals except the most unreactive ones, such as platinum and gold, are attacked by it. Nitric acid also does a good job of oxidizing organic compounds, so it is wise to be especially careful when working with this acid in the laboratory. Very serious accidents have occurred when inexperienced people have used concentrated nitric acid around organic substances.

Hot Concentrated Sulfuric Acid: Another Oxidizing Acid

In a dilute solution, the sulfate ion of sulfuric acid has little tendency to serve as an oxidizing agent. However, if the sulfuric acid is both concentrated and hot, it becomes a fairly potent oxidizer. For example, copper is not bothered by cool dilute H_2SO_4, but it is attacked by hot concentrated H_2SO_4 according to the following equation:

$$Cu + 2H_2SO_4(\text{hot, conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Because of this oxidizing ability, hot concentrated sulfuric acid can be very dangerous. The liquid is viscous and can stick to the skin, causing severe burns.

Practice Exercises

6.20 | Write the balanced half-reactions for the reaction of zinc with hydrogen ions. (*Hint:* Be sure to place the electrons on the correct sides of the half-reactions.)

6.21 | Write balanced molecular, ionic, and net ionic equations for the reaction of hydrochloric acid with (a) magnesium and (b) aluminum. (Both are oxidized by hydrogen ions.)

6.22 | Hot concentrated sulfuric acid is reduced to hydrogen sulfide by hydroiodic acid, which forms iodine. Balance the equation that describes the reaction.

$$H_2SO_4 + HI \longrightarrow H_2S + I_2$$

6.4 | Redox Reactions of Metals

The formation of hydrogen gas in the reaction of a metal with an acid is a special case of a more general phenomenon—one element displacing (pushing out) another element from a compound by means of a redox reaction. In the case of a metal–acid reaction, it is the metal that displaces hydrogen from the acid, changing $2H^+$ to H_2.

Another reaction of this same general type occurs when one metal displaces another metal from its compounds, and is illustrated by the experiment shown in Figure 6.5. Here we see a brightly polished strip of metallic zinc that is dipped into a solution of copper sulfate. After the zinc is in the solution for a while, a reddish brown deposit of metallic copper forms on the zinc, and if the solution were analyzed, we would find that it now contains zinc ions, as well as some remaining unreacted copper ions.

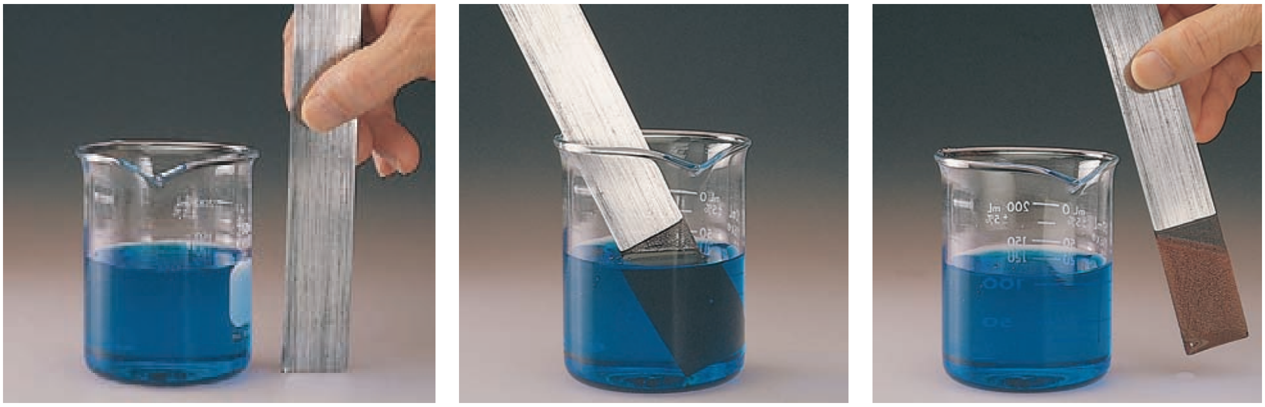


Figure 6.5 | **The reaction of zinc with copper ion.** (*Left*) A piece of shiny zinc next to a beaker containing a copper sulfate solution. (*Center*) When the zinc is placed in the solution, copper ions are reduced to the free metal while the zinc dissolves. (*Right*) After a while the zinc becomes coated with a red-brown layer of copper. Notice that the solution is a lighter blue than before, showing that some of the copper ions have left the solution. *(Michael Watson)*

The results of this experiment can be summarized by the following net ionic equation:

■ Sulfate ion is a spectator ion in this reaction.

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Cu}(s) + \mathrm{Zn}^{2+}(aq)$$

Metallic zinc is oxidized as copper ion is reduced. In the process, Zn^{2+} ions have taken the place of the Cu^{2+} ions, so a solution of copper sulfate is changed to a solution of zinc sulfate. An atomic-level view of what's happening at the surface of the zinc during the reaction is depicted in Figure 6.6. A reaction such as this, in which one element replaces another in a compound, is sometimes called a **single replacement reaction**.

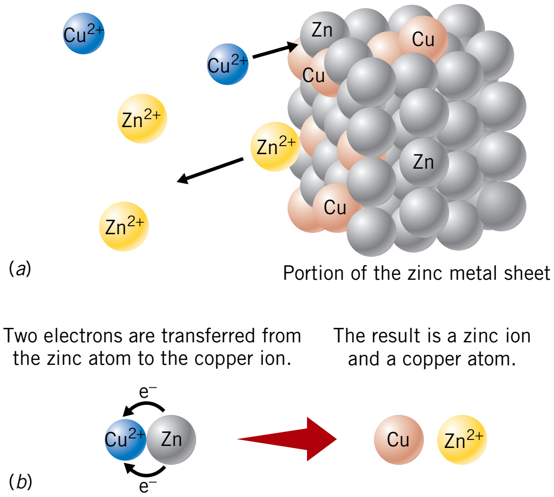

Cu2+
Cu2+
Zn
Cu
Cu
Zn2+
Zn2+
Zn
Cu
Zn2+
(a)
Portion of the zinc metal sheet
Two electrons are transferred from the zinc atom to the copper ion.
The result is a zinc ion and a copper atom.
e−
Cu2+
Zn
e−
Cu
Zn2+
(b)

Figure 6.6 | **An atomic-level view of the reaction of copper ions with zinc.** *(a)* Copper ions (blue) collide with the zinc surface, where they pick up electrons from zinc atoms (gray). The zinc atoms become zinc ions (yellow) and enter the solution. The copper ions become copper atoms (red-brown) and stick to the surface of the zinc. (For clarity, the water molecules of the solution and the sulfate ions are not shown.) *(b)* A close-up view of the exchange of electrons that leads to the reaction.

Activity Series of Metals

Activity series of metal

In the reaction of zinc with copper ion, the more "active" zinc displaces the less "active" copper in a compound, where we have used the word *active* to mean "easily oxidized." This is actually a general phenomenon: *an element that is more easily oxidized will displace one that is less easily oxidized from its compounds*. By comparing the relative ease of oxidation of various metals using experiments like the one pictured in Figure 6.5, we can arrange metals in order of their ease of oxidation. This yields the **activity series** shown in Table 6.3. In this table, metals at the bottom are more easily oxidized (are more active) than those at the top. *This means that a given element will be displaced from its compounds by any metal below it in the table.*

Table 6.3 Activity Series for Some Metals (and Hydrogen)

Activity	Element	Oxidation Product
Least Active Do not react with nonoxidizing acids	Gold	Au^{3+}
	Mercury	Hg^{2+}
	Silver	Ag^{+}
	Copper	Cu^{2+}
	HYDROGEN	H^{+}
React with nonoxidizing acids	Lead	Pb^{2+}
	Tin	Sn^{2+}
	Cobalt	Co^{2+}
	Cadmium	Cd^{2+}
	Iron	Fe^{2+}
	Chromium	Cr^{3+}
	Zinc	Zn^{2+}
	Manganese	Mn^{2+}
	Aluminum	Al^{3+}
	Magnesium	Mg^{2+}
React with water to produce hydrogen	Sodium	Na^{+}
	Calcium	Ca^{2+}
	Strontium	Sr^{2+}
	Barium	Ba^{2+}
	Cesium	Cs^{+}
	Potassium	K^{+}
Most Active	Rubidium	Rb^{+}

Increasing ease of oxidation of the metal

Increasing ease of reduction of the ion

Notice that we have included hydrogen in the activity series. Metals below hydrogen in the series can displace hydrogen from solutions containing H^+. These are the metals that are capable of reacting with nonoxidizing acids. On the other hand, metals above hydrogen in the table do not react with acids having H^+ as the strongest oxidizing agent.

Metals at the very bottom of the table are very easily oxidized and are extremely strong reducing agents. They are so reactive, in fact, that they are able to reduce the hydrogen in water molecules. Sodium, for example, reacts vigorously (see Figure 6.7).

$$2Na(s) + 2H_2O \longrightarrow H_2(g) + 2NaOH(aq)$$

For metals below hydrogen in the activity series, there's a parallel between the ease of oxidation of the metal and the speed with which it reacts with H^+. For example, in

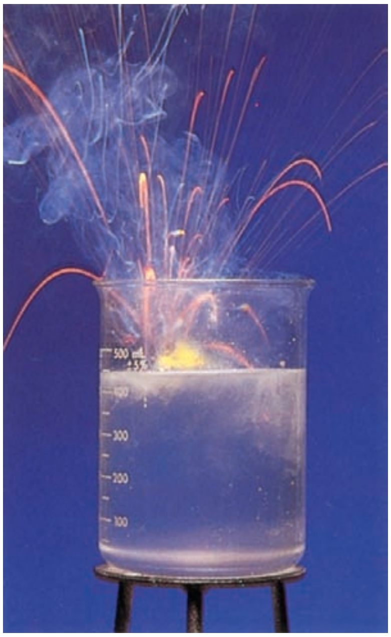
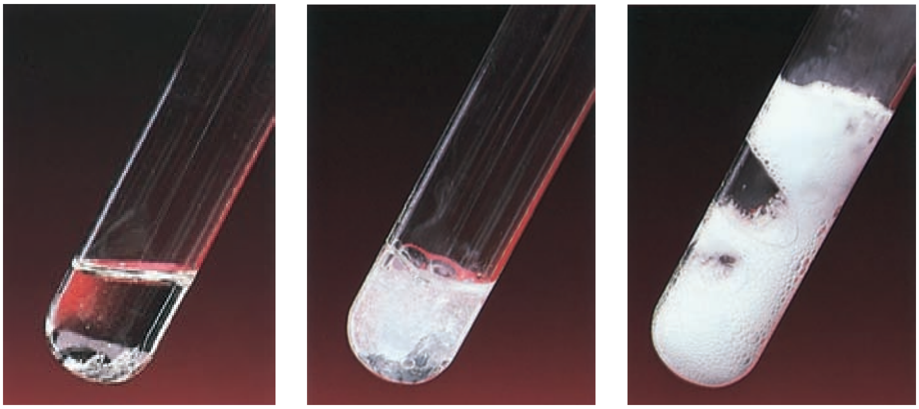


Figure 6.7 | **Metallic sodium reacts violently with water.** The heat of the reaction ignites the sodium metal, which can be seen burning and sending sparks from the surface of the water. In the reaction, sodium is oxidized to Na^+ and water molecules are reduced to give hydrogen gas and hydroxide ions. When the reaction is over, the solution contains sodium hydroxide. *(OPC, Inc.)*



$2HCl(aq) + Fe(s) \longrightarrow FeCl_2(aq) + H_2(g)$

$2HCl(aq) + Zn(s) \longrightarrow ZnCl_2(aq) + H_2(g)$

$2HCl(aq) + Mg(s) \longrightarrow MgCl_2(aq) + H_2(g)$

Figure 6.8 | **The relative ease of oxidation of metals as demonstrated by their reaction with hydrogen ions of an acid.** The products are hydrogen gas and the metal ion in solution. All three test tubes contain $HCl(aq)$ at the same concentration. The first also contains pieces of iron, the second, pieces of zinc, and the third, pieces of magnesium. Among these three metals, the ease of oxidation increases from iron to zinc to magnesium. *(OPC, Inc.)*

Figure 6.8, we see samples of iron, zinc, and magnesium reacting with solutions of hydrochloric acid. In each test tube the initial HCl concentration is the same, but we see that the magnesium reacts more rapidly than zinc, which reacts more rapidly than iron. You can see that this matches the order of reactivity in Table 6.3—namely, magnesium is more easily oxidized than zinc, which is more easily oxidized than iron.

Using the Activity Series to Predict Reactions

The activity series in Table 6.3 makes it possible to predict the outcome of single replacement redox reactions, as illustrated in Examples 6.7 and 6.8.

Example 6.7

Using the Activity Series

What will happen if an iron nail is dipped into a solution containing copper(II) sulfate? If a reaction occurs, write its molecular equation.

■ **Analysis:** Before deciding what *will* happen, we have to consider, what *could* happen? If a chemical reaction were to occur, iron would have to react with the copper sulfate. A *metal* possibly reacting with the *salt of another metal?* This suggests the possibility of a single replacement reaction.

■ **Assembling the Tools:** The tool we use to predict such reactions is the activity series of the metals in Table 6.3.

Solution: Examining Table 6.3, we see that iron is below copper. This means iron is more easily oxidized than copper, so we expect metallic iron to displace copper ions from the solution. *A reaction will occur.* (We've answered one part of the question.) The formula for copper(II) sulfate is $CuSO_4$. To write an equation for the reaction, we have to know the final oxidation state of the iron. In the table, this is indicated as +2, so the Fe atoms change to Fe^{2+} ions. To write the formula of the salt in the solution we pair Fe^{2+} with SO_4^{2-} to give $FeSO_4$. Copper(II) ions are reduced to copper atoms.

Our analysis told us that a reaction *will* occur and it also gave us the products, so the equation is

$$\mathrm{Fe}(s) + \mathrm{CuSO_4}(aq) \longrightarrow \mathrm{Cu}(s) + \mathrm{FeSO_4}(aq)$$

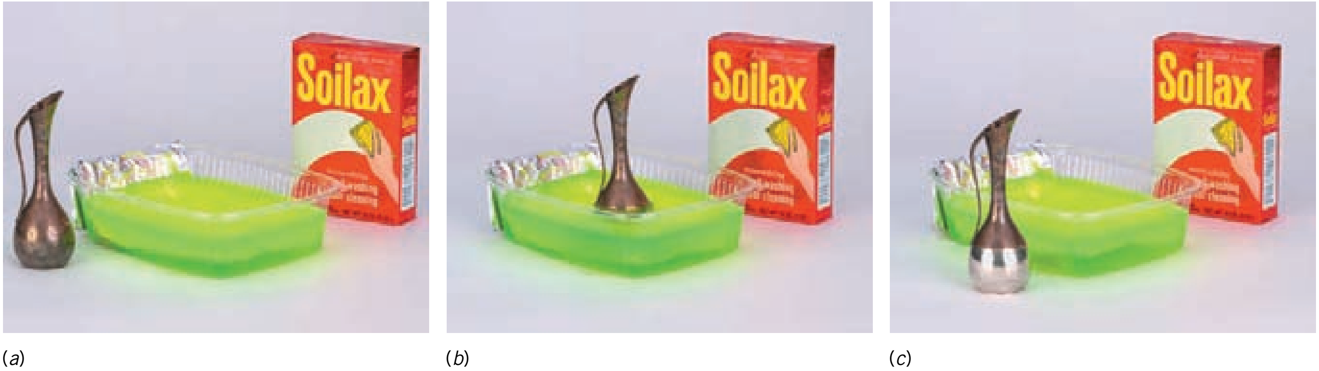
Is the Answer Reasonable? We can check the activity series again to be sure we've reached the correct conclusion, and we can check to be sure the equation we've written has the correct formulas and is balanced correctly. Doing this confirms that we've got the right answers.

CHEMISTRY OUTSIDE THE CLASSROOM 6.1

Polishing Silver—The Easy Way

Using an active metal to reduce a compound of a less active metal has a number of practical applications. One that is handy around the home is using aluminum to remove the tarnish from silver. Generally, silver tarnishes by a gradual reaction with hydrogen sulfide, present in very small amounts in the air. The product of the reaction is silver sulfide, Ag_2S, which is black and forms a dull film over the bright metal. Polishing a silver object using a mild abrasive restores the shine, but it also gradually removes silver from the object as the silver sulfide is rubbed away.

An alternative method, and one that requires little effort, involves lining the bottom of a sink with aluminum foil, adding warm water and detergent (which acts as an electrolyte), and then submerging the tarnished silver object in the detergent–water mixture and placing it in contact with the aluminum (Figure 1). In a short time, the silver sulfide is reduced, restoring the shine and depositing the freed silver metal on the object. As this happens, a small amount of the aluminum foil is oxidized and caused to dissolve. Besides requiring little physical effort, this silver polishing technique doesn't remove silver from the object being polished. Also, *the silver, considered a heavy metal, is being kept out of the water.*



(*a*) (*b*) (*c*)

Figure 1 Using aluminum to remove tarnish from silver. (*a*) A badly tarnished silver vase stands next to a container of detergent (Soilax) dissolved in water. The bottom of the container is lined with aluminum foil. (*b*) The vase, shown partly immersed in the detergent, rests on the aluminum foil. (*c*) After a short time, the vase is removed, rinsed with water, and wiped with a soft cloth. Where the vase was immersed in the liquid, much of the tarnish has been reduced to metallic silver. *(Andy Washnik)*

Example 6.8
Using the Activity Series

What happens if an iron nail is dipped into a solution of aluminum sulfate? If a reaction occurs, write the molecular equation.

Analysis: Once again, we have to realize that we're looking for a potential single replacement reaction.

Assembling the Tools: We will use the activity series of the metals in Table 6.3 as our tool to solve this problem.

Solution: Scanning the activity series, we see that aluminum metal is *more* easily oxidized than iron metal. This means that aluminum atoms would be able to displace iron ions from an iron compound. But it also means that iron atoms cannot displace aluminum ions from its compounds, and iron *atoms* plus aluminum *ions* are what we're given. Our analysis has told us that iron atoms will not reduce aluminum ions, so we must conclude that no reaction can occur.

$$\text{Fe}(s) + \text{Al}_2(\text{SO}_4)_3(aq) \longrightarrow \text{no reaction}$$

Is the Answer Reasonable? Checking the activity series again, we are confident we've come to the correct answer. In writing the equation, we've also been careful to correctly write the formula of aluminum sulfate.

Practice Exercises

6.23 | Suppose an aqueous mixture is prepared containing magnesium sulfate ($MgSO_4$), copper(II) sulfate ($CuSO_4$), metallic magnesium, and metallic copper. What reaction, if any, will occur? (*Hint:* What reactions could occur?)

6.24 | Write a chemical equation for the reaction that will occur, if any, when (a) aluminum metal is added to a solution of copper(II) chloride and (b) silver metal is added to a solution of magnesium sulfate. If no reaction will occur, write "no reaction" in place of the products.

6.5 | Molecular Oxygen as an Oxidizing Agent

Oxygen is a plentiful chemical; it's in the air and available to anyone who wants to use it, chemist or not. Furthermore, O_2 is a very reactive oxidizing agent, so its reactions have been well studied. When these reactions are rapid, with the evolution of light and heat, we call them **combustion**. The products of reactions with oxygen are generally oxides—*molecular oxides* when oxygen reacts with nonmetals and *ionic oxides* when oxygen reacts with metals.

Oxidation of Organic Compounds

Experience has taught you that certain materials burn. For example, if you had to build a fire to keep warm, you no doubt would look for combustible materials like twigs, logs, or other pieces of wood to use as fuel. The car you drive is probably powered by the combustion of gasoline. Wood and gasoline are examples of substances or mixtures of substances that chemists call *organic compounds*—compounds whose structures are determined primarily by the linking together of carbon atoms. When organic compounds burn, the products of the reactions are usually easy to predict.

Hydrocarbons as Fuels

Fuels such as natural gas, gasoline, kerosene, heating oil, and diesel fuel are examples of *hydrocarbons*—compounds containing only the elements carbon and hydrogen. Natural gas is composed principally of methane, CH_4. Gasoline is a mixture of hydrocarbons, the most familiar of which is octane, C_8H_{18}. Kerosene, heating oil, and diesel fuel are mixtures of hydrocarbons in which the molecules contain even more atoms of carbon and hydrogen. When hydrocarbons are burned in air, besides water, a mixture of carbon-containing products are formed, such as carbon dioxide, carbon monoxide, and carbon as soot. If the conditions are carefully managed, the products can be controlled.

TOOLS

Hydrocarbon combustion with a plentiful supply of O_2

When hydrocarbons burn in a ***plentiful*** *supply of oxygen, the products of combustion are mainly carbon dioxide and water.* Thus, methane and octane combine with oxygen according to the equations

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Many people don't realize that water is one of the products of the combustion of hydrocarbons, even though they have seen evidence for it. Perhaps you've seen clouds of condensed water vapor coming from the exhaust pipes of automobiles on cold winter days, or you may have noticed that shortly after you first start a car, drops of water fall from the exhaust pipe. This is water that has been formed during the combustion of the gasoline. Similarly, the "smokestacks" of power stations release clouds of condensed water vapor (Figure 6.9), which is often mistaken for smoke from fires used to generate power to make electricity. Actually, many of today's power stations produce very little smoke because they burn natural gas instead of coal.

■ You can tell whether smoke or water vapor is coming from a smokestack. If the cloud is steam, there will be a clear region just above the smokestack. If the emissions are smoke, no clear region will exist.

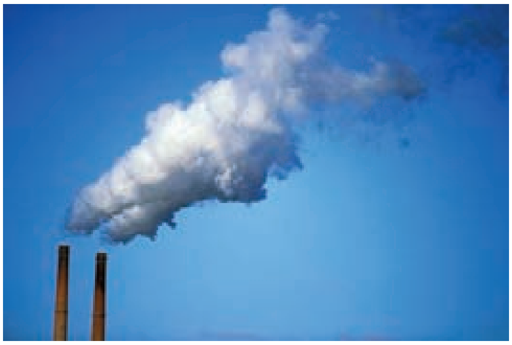


Figure 6.9 | **Water is a product of the combustion of hydrocarbons.** Here we see clouds of condensed water vapor coming from the stacks of an oil-fired electric generating plant during the winter. *(PictureNet/©Corbis)*

TOOLS

Hydrocarbon combustion with a limited supply of O_2

When the supply of oxygen is somewhat restricted during the combustion of a hydrocarbon, some of the carbon is converted to carbon monoxide. The formation of CO is a pollution problem associated with the use of gasoline engines, as you may know.

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O \qquad \text{(in a limited oxygen supply)}$$

TOOLS

Hydrocarbon combustion with an extremely limited supply of O_2

When the oxygen supply is extremely limited, only the hydrogen of a hydrocarbon mixture is converted to the oxide (water) and the carbon atoms emerge as elemental carbon. For example, when a candle burns, the fuel is a high-molecular-weight hydrocarbon (e.g., $C_{20}H_{42}$) and incomplete combustion forms tiny particles of carbon that glow brightly, creating the candle's light. If a cold surface is held in the flame, the unburned carbon deposits, as seen in Figure 6.10.

An important commercial reaction is the incomplete combustion of methane in a very limited oxygen supply, which follows the equation

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$
$$\text{(in a very limited oxygen supply)}$$

■ In all three of these reactions of hydrocarbons with oxygen, some of the other carbon products are formed. However, we will assume that just one product is formed: for a plentiful supply of oxygen, carbon dioxide; for a limited supply of oxygen, carbon monoxide; and for an extremely limited supply of oxygen, carbon.

The carbon that forms is very finely divided and would be called *soot* by almost anyone observing the reaction. Nevertheless, such soot has considerable commercial value when collected and marketed under the name *lampblack*. This sooty form of carbon is used to manufacture inks and tons of it are used in the production of rubber tires, where it serves as a binder and a filler. When soot from incomplete combustion is released into air, its tiny particles constitute a component of air pollution referred to as *particulates,* which contribute to the haziness of smog.

■ This finely divided form of carbon is also called *carbon black.*

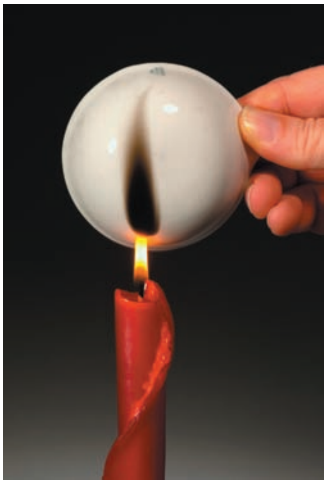


Figure 6.10 | **Incomplete combustion of a hydrocarbon.** The bright yellow color of a candle flame is caused by glowing particles of elemental carbon. Here we see that a black deposit of carbon is formed when the flame contacts a cold porcelain surface. *(Andy Washnik)*

Combustion of Organic Compounds That Contain Oxygen

Earlier we mentioned that you might choose wood to build a fire. The chief combustible ingredient in wood is cellulose, a fibrous material that gives plants their structural strength. Cellulose is composed of the elements carbon, hydrogen, and oxygen. Each cellulose molecule consists of many small, identical groups of atoms that are linked together to form a very long molecule, although the lengths of the molecules differ. For this reason we cannot specify a molecular formula for cellulose. Instead, we use the empirical formula, $C_6H_{10}O_5$, which represents the small, repeating "building block" units in large cellulose molecules. When cellulose burns, the products are mainly carbon dioxide and water. The only difference between its reaction and the reaction of a hydrocarbon with oxygen is that some of the oxygen in the products comes from the cellulose.

■ The formula for cellulose can be expressed as $(C_6H_{10}O_5)_n$, which indicates that the molecule contains the $C_6H_{10}O_5$ unit repeated some large number *n* times.

$$C_6H_{10}O_5 + 6O_2 \longrightarrow 6CO_2 + 5H_2O$$

TOOLS Combustion of an organic compound containing C, H, and O

The complete combustion of all other organic compounds containing only carbon, hydrogen, and oxygen produces the same products, CO_2 and H_2O, and follows similar equations.

■ These reactions can also be balanced using the ion–electron method, with oxygen going to water and the organic compound going to carbon dioxide, carbon monoxide, or carbon, depending on the amount of oxygen available.

Burning Organic Compounds That Contain Sulfur

A major pollution problem is caused by the release into the atmosphere of sulfur dioxide formed by the combustion of fuels that contain sulfur or its compounds. *The products of the combustion of organic compounds of sulfur are carbon dioxide, water, and sulfur dioxide.* A typical reaction is

$$2C_2H_5SH + 9O_2 \longrightarrow 4CO_2 + 6H_2O + 2SO_2$$

TOOLS Combustion of an organic compound containing sulfur

A solution of sulfur dioxide in water is acidic, and when rain falls through polluted air it picks up SO_2 and becomes "acid rain." Some SO_2 is also oxidized to SO_3, which reacts with moisture to give H_2SO_4, making the acid rain even more acidic.

Practice Exercises

6.25 | Write a balanced chemical equation for the combustion of candle wax, $C_{20}H_{42}$, in a very limited supply of oxygen. (*Hint:* What happens to methane under these conditions?)

6.26 | Write a balanced equation for the combustion of isoprene, C_5H_8, in an abundant supply of oxygen. Isoprene is emitted by trees and is used in the production of synthetic rubber.

6.27 | Ethanol, C_2H_5OH, is now mixed with gasoline, and the mixture is sold under the name *gasohol*. Write a chemical equation for the complete combustion of ethanol.

Reactions of Metals with Oxygen

We don't often think of metals as undergoing combustion, but have you ever lit a sparkler on the Fourth of July? The source of light is the reaction of the metal magnesium with oxygen. A close look at a fresh flashbulb reveals a fine web of thin magnesium wire within the glass envelope (see Figure 6.11). The wire is surrounded by an atmosphere of oxygen, a clear colorless gas. When the flashbulb is used, a small electric current surges through the thin wire, causing it to become hot enough to ignite, and it burns rapidly in the oxygen atmosphere. The equation for the reaction is

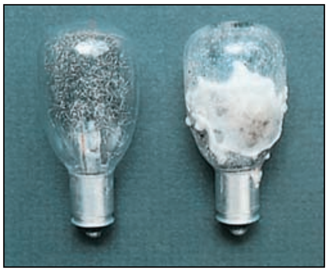


Figure 6.11 | **A flashbulb, before and after firing.** Fine magnesium wire in an atmosphere of oxygen fills the flashbulb at the left. After being used (*right*), the interior of the bulb is coated with a white film of magnesium oxide. *(Robert Capece)*

$$2Mg + O_2 \longrightarrow 2MgO$$

Most metals react directly with oxygen, although not so spectacularly, and usually we refer to the reaction as **corrosion** or **tarnishing** because the oxidation products dull the shiny metal surface. Iron, for example, is oxidized fairly easily, especially in the presence of moisture. As you know, under these conditions the iron corrodes—it rusts. Rust is a form of iron(III) oxide, Fe_2O_3, that also contains an appreciable amount of absorbed water. The formula for rust is therefore normally given as $Fe_2O_3 \cdot xH_2O$ to indicate its somewhat variable composition. Although the rusting of iron is a slow reaction, the combination of iron with oxygen can be speeded up if the metal is heated to a very high temperature under a stream of pure O_2 (see Figure 6.12).

An aluminum surface, unlike that of iron, is not noticeably dulled by the reaction of aluminum with oxygen. Aluminum is a common metal found around the home in uses ranging from aluminum foil to aluminum window frames, and it surely appears shiny. However, aluminum is a rather easily oxidized metal, as can be seen from its position in the activity series (Table 6.3). A *freshly* exposed surface of the metal does react very quickly with oxygen and becomes coated with a very thin film of aluminum oxide, Al_2O_3, so thin that it doesn't obscure the shininess of the metal beneath. Fortunately, the oxide coating adheres very tightly to the surface of the metal and makes it very difficult for additional oxygen to combine with the aluminum. Therefore, further oxidation of aluminum occurs very slowly. On the other hand, powdered aluminum, which has a large surface area, reacts violently when ignited and is part of the propellant in the booster rockets for the space shuttle.

Practice Exercises

6.28 | Write a balanced chemical equation for the reaction of molecular oxygen with strontium metal to form the oxide. (*Hint:* Strontium, Sr, is in the same group in the periodic table as calcium.)

6.29 | The oxide formed in the reaction shown in Figure 6.12 is iron(III) oxide. Write a balanced chemical equation for the reaction.

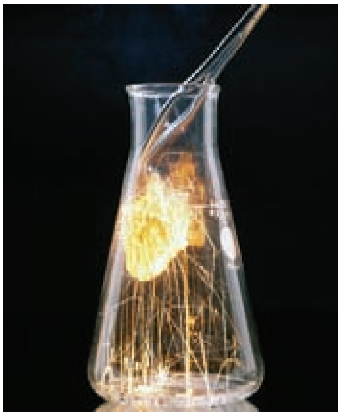


Figure 6.12 | **Hot steel wool burns in oxygen.** The reaction of hot steel wool with oxygen speeds up the oxidation process and the sparks and flames result. *(© 1993 Richard Megna/Fundamental Photographs)*

Reaction of Nonmetals with Oxygen

Most nonmetals combine as readily with oxygen as do the metals, and their reactions usually occur rapidly enough to be described as combustion. To most people, the most important nonmetal combustion reaction is that of carbon because the reaction is a source of heat. Coal and charcoal, for example, are common carbon fuels. Coal is used worldwide in large amounts to generate electricity, and charcoal is a popular fuel for grilling hamburgers. If plenty of oxygen is available, the combustion of carbon gives CO_2, but when the supply of O_2 is limited, some CO forms as well. Manufacturers that package charcoal briquettes, therefore, print a warning on the bag that the charcoal shouldn't be used indoors for cooking or heating because of the danger of carbon monoxide poisoning.

WARNING
CARBON MONOXIDE HAZARD
Burning charcoal inside can kill you. It gives off carbon monoxide, which has no odor.
NEVER burn charcoal inside homes, vehicles or tents.

The label on a bag of charcoal displays a warning about carbon monoxide. *(Andy Washnik)*

Sulfur is another nonmetal that burns readily in oxygen to produce sulfur dioxide. One important use for this reaction is in the manufacture of sulfuric acid. The first step in the manufacturing process is the combustion of sulfur to produce sulfur dioxide. In addition, sulfur dioxide also forms when sulfur compounds burn, and the presence of sulfur and sulfur compounds in coal and petroleum is a major source of air pollution. Power plants that burn coal are making strides to remove the SO_2 from their exhausts.

Nitrogen also reacts with oxygen to form nitrogen oxides: NO, NO_2, N_2O, N_2O_3, N_2O_4, and N_2O_5. Nitrogen oxide and nitrogen dioxide are formed when nitrogen and oxygen are heated to high enough temperatures and pressures such as the temperature of a car engine. Dinitrogen oxide, also known as nitrous oxide or laughing gas, is used as an anesthetic by dentists and as the propellant in canned whipped cream, Reddi-wip®.

6.6 | Stoichiometry of Redox Reactions

In general, working stoichiometry problems involving redox reactions follows the same principles we've applied to other reactions. The principal difference is that the chemical equations are more complex. Nevertheless, once we have a balanced equation, the moles of substances involved in the reaction are related by the coefficients in the balanced equation.

Because so many reactions involve oxidation and reduction, it should not be surprising that they have useful applications in the lab. Some redox reactions are especially useful in chemical analyses, particularly in titrations. In acid–base titrations, we often need a specific indicator for each reaction to detect the end point. However, there are no simple indicators that can be used to conveniently detect the end points in redox titrations. Conveniently, there are a few oxidizing agents that are highly colored and can act as their own indicator, so we have to rely on color changes among the reactants themselves.

One of the most useful reactants for redox titrations is potassium permanganate, $KMnO_4$, especially when the reaction can be carried out in an acidic solution. Permanganate ion is a powerful oxidizing agent, so it oxidizes most substances that are capable of being oxidized. That's one reason why it is used. Especially important, though, is the fact that the MnO_4^- ion has an intense purple color and its reduction product in acidic solution is the almost colorless Mn^{2+} ion. Therefore, when a solution of $KMnO_4$ is added from a buret to a solution of a reducing agent, the chemical reaction that occurs forms a nearly colorless product. This is illustrated in Figure 6.13, where we see a solution of $KMnO_4$ being poured into an acidic solution containing Fe^{2+}. As the $KMnO_4$ solution is added, the purple color continues to be destroyed as long as there is any reducing agent left. In a titration, after the last trace of the reducing agent has been consumed, the MnO_4^- ion in the next drop of titrant has nothing to react with, so it colors the solution pink. This signals the end of the titration. In this way, permanganate ion serves as its own indicator in redox titrations. The next multi-concept problem illustrates a typical analysis using $KMnO_4$ in a redox titration.

■ In concentrated solutions, MnO_4^- is purple, but dilute solutions of the ion appear pink.

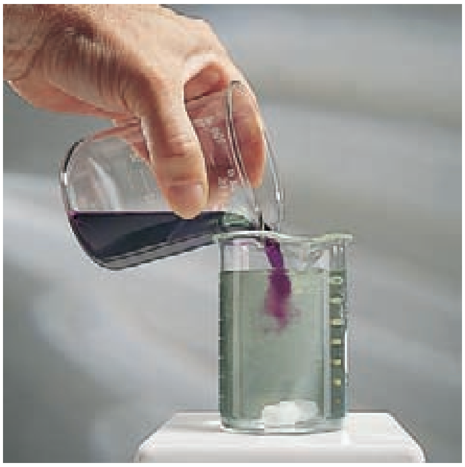


Figure 6.13 | **Reduction of MnO_4^- by Fe^{2+}.** A solution of $KMnO_4$ is added to a stirred acidic solution containing Fe^{2+}. The reaction oxidizes the pale blue-green Fe^{2+} to Fe^{3+}, while the MnO_4^- is reduced to the almost colorless Mn^{2+} ion. The purple color of the permanganate will continue to be destroyed until all of the Fe^{2+} has reacted. Only then will the iron-containing solution take on a pink or purple color. This ability of MnO_4^- to signal the completion of the reaction makes it especially useful in redox titrations, where it serves as its own indicator. *(Andy Washnik)*

Analyzing and Solving Multi-Concept Problems

All the iron in a 2.00 g sample of an iron ore was dissolved in an acidic solution and converted to Fe^{2+}, which was then titrated with 0.100 *M* $KMnO_4$ solution. In the titration the iron was oxidized to Fe^{3+}. The titration required 27.45 mL of the $KMnO_4$ solution to reach the end point.

(a) How many grams of iron were in the sample?
(b) What was the percentage of iron in the sample?
(c) If the iron was present in the sample as Fe_2O_3, what was the percentage by mass of Fe_2O_3 in the sample?

Analysis This problem has several parts to it, so to solve it we will divide it into three parts. The first will be to construct a balanced equation to get the correct stoichiometry, the second will be to find the mass of iron and the percentage of iron in the sample, and the third will be to find the percentage by mass of the Fe_2O_3. In the final two parts, we will use tools we learned in Chapters 4 and 5, as well as tools from this chapter.

PART 1

Assembling the Tools: To start with, let's use the method for balancing redox reactions in acidic solutions as a tool, even though the question does not explicitly state that it is needed.

Solution: The compound $KMnO_4$ provides MnO_4^-, and the K^+ is a spectator ion and is not included in balancing the equation. The skeleton equation for the reaction is

$$Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

Balancing it by the ion–electron method for acidic solutions gives

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

PART 2

Assembling the Tools: With this information, let's look over the tools we'll use to answer the first two questions. We'll tackle the calculation of percent Fe_2O_3 afterward.

- Molarity and volume of the $KMnO_4$: These will give us moles of $KMnO_4$ used in the titration [remember: volume (in liters) × molarity = moles].
- Coefficients of the equation: These permit us to find moles of iron from the moles of $KMnO_4$ used.
- Molar mass of iron: This lets us calculate the mass of iron in the sample from moles of iron.
- Equation to calculate the percentage of iron: $\%Fe = \dfrac{\text{g Fe}}{\text{g sample}} \times 100\%$.

Solution: The number of moles of MnO_4^- consumed in the reaction is calculated from the volume of the solution used in the titration and its concentration.

$$0.02745\ \cancel{\text{L MnO}_4^-\text{ soln}} \times \frac{0.100\text{ mol MnO}_4^-}{1.00\ \cancel{\text{L MnO}_4^-\text{ soln}}} = 0.002745\text{ mol MnO}_4^-$$

Next, we use the coefficients of the equation to calculate the number of moles of Fe^{2+} that reacted. The balanced chemical equation tells us five moles of Fe^{2+} react per mole of MnO_4^- consumed.

$$0.002745\ \cancel{\text{mol MnO}_4^-} \times \frac{5\text{ mol Fe}^{2+}}{1\ \cancel{\text{mol MnO}_4^-}} = 0.01372\text{ mol Fe}^{2+}$$

This is the number of moles of iron in the ore sample, so the mass of iron in the sample is

$$0.01372\ \cancel{\text{mol Fe}} \times \frac{55.845\text{ g Fe}}{\cancel{1\text{ mol Fe}}} = 0.766\text{ g Fe}$$

Next, we calculate the percentage of iron in the sample, which is the mass of iron divided by the mass of the sample, all multiplied by 100%.

$$\%\text{ Fe} = \frac{\text{mass of Fe}}{\text{mass of sample}} \times 100\%.$$

Substituting gives

$$\%\text{ Fe} = \frac{0.766\text{ g Fe}}{2.00\text{ g sample}} \times 100\% = 38.3\%\text{ Fe}$$

The answer to part (b) is that the sample is 38.3% iron.

PART 3

Assembling the Tools: In Part 2 we determined that 0.0137 mol Fe had reacted. How many moles of Fe_2O_3 would have contained this number of moles of iron? Once we know this, we can calculate the mass of the Fe_2O_3 and the percentage of Fe_2O_3 in the original sample.
The tools we'll use in solving this part of the problem are:

- The chemical formula, Fe_2O_3: The formula relates moles of iron to moles Fe_2O_3.
- The molar mass of Fe_2O_3: This lets us calculate the mass of Fe_2O_3.
- The formula for calculating the percentage of Fe_2O_3: $\%\ Fe_2O_3 = \frac{\text{g Fe}_2\text{O}_3}{\text{g sample}} \times 100\%$.

Solution: (c) The chemical formula for the iron oxide gives us

$$1\text{ mol Fe}_2\text{O}_3 \Leftrightarrow 2\text{ mol Fe}$$

This provides the conversion factor we need to determine how many moles of Fe_2O_3 were present in the sample. Working with the number of moles of Fe,

$$0.0137\ \cancel{\text{mol Fe}} \times \frac{1\text{ mole Fe}_2\text{O}_3}{2\ \cancel{\text{mol Fe}}} = 0.00685\text{ mol Fe}_2\text{O}_3$$

This is the number of moles of Fe_2O_3 in the sample. The formula mass of Fe_2O_3 is 159.69 g mol^{-1}, so the mass of Fe_2O_3 in the sample was

$$0.00685\ \cancel{\text{mol Fe}_2\text{O}_3} \times \frac{159.69\text{ g Fe}_2\text{O}_3}{1\ \cancel{\text{mol Fe}_2\text{O}_3}} = 1.094\text{ g Fe}_2\text{O}_3$$

Finally, the percentage of Fe_2O_3 in the sample was

$$\% \ Fe_2O_3 = \frac{1.094 \text{ g } Fe_2O_3}{2.00 \text{ g sample}} \times 100\% \ = 54.7\% \ Fe_2O_3$$

The ore sample contained 54.8% Fe_2O_3.

■ **Are the Answers Reasonable?** For the first part, which involved balancing redox reactions, there are two steps to making sure the reaction is properly balanced: checking mass and charge. For the mass, we have to make sure each side of the equation has the same number of atoms of each element, and for the charge we need to check that the net charge is the same on both sides.

For the second part, we can use some approximate arithmetic to estimate the answer. In the titration we used approximately 30 mL, or 0.030 L, of the $KMnO_4$ solution, which is 0.10 *M*. Multiplying these tells us we've used approximately 0.003 mol of $KMnO_4$. From the coefficients of the equation, five times as many moles of Fe^{2+} react, so the amount of Fe in the sample is approximately $5 \times 0.003 = 0.015$ mol. The atomic mass of Fe is about 55 g/mol, so the mass of Fe in the sample is approximately $0.015 \times 55 = 0.8$ g. Our answer (0.766 g) is reasonable.

For the last part, we've noted that the amount of Fe in the sample is approximately 0.015 mol. The amount of Fe_2O_3 that contains this much Fe is 0.0075 mol. The formula mass of Fe_2O_3 is about 160, so the mass of Fe_2O_3 in the sample was approximately $0.0075 \times 160 = 1.2$ g, which isn't too far from the mass we obtained (1.095 g). Since 1.09 g is about half of the total sample mass of 2.00 g, the sample was approximately 50% Fe_2O_3, in agreement with the answer we obtained.

Summary

Oxidation–Reduction. **Oxidation** is the loss of electrons or an algebraic increase in oxidation number; **reduction** is the gain of electrons or an algebraic decrease in oxidation number. Both always occur together in **redox** reactions. The substance oxidized is the **reducing agent;** the substance reduced is the **oxidizing agent. Oxidation numbers** are a bookkeeping device that we use to follow changes in redox reactions. They are assigned according to the rules on page 217. The term **oxidation state** is equivalent to oxidation number. These terms are summarized in Table 6.1.

Ion–Electron Method. In a balanced redox equation, the number of electrons gained by one substance is always equal to the number lost by another substance. This fact forms the basis for the **ion–electron method**, which provides a systematic method for deriving a net ionic equation for a redox reaction in aqueous solution. According to this method, the *skeleton* net ionic equation is divided into two **half-reactions,** which are balanced separately before being recombined to give the final balanced net ionic equation. For reactions in basic solutions the equation is balanced as if it occurred in an acidic solution, and then the balanced equation is converted to its proper form for basic solutions by adding an appropriate number of OH^- to both sides and canceling H_2O if possible.

Metal–Acid Reactions. In **nonoxidizing acids,** the strongest oxidizing agent is H^+ (Table 6.2). The reaction of a metal with a nonoxidizing acid gives hydrogen gas and a salt of the acid. Only metals more active than hydrogen react this way. These are metals that are located below hydrogen in the **activity series** (Table 6.3). **Oxidizing acids,** like HNO_3, contain an anion that is a stronger oxidizing agent than H^+, and they are able to oxidize many metals that nonoxidizing acids cannot.

Metal–Displacement Reactions. If one metal is more easily oxidized than another, it can displace the other metal from its compounds by a redox reaction. Such reactions are sometimes called **single replacement reactions.** Atoms of the more active metal become ions; ions of the less active metal generally become atoms. In this manner, any metal in the **activity series** can displace any of the others above it in the series from their compounds.

Oxidations by Molecular Oxygen. **Combustion** is the rapid reaction of a substance with oxygen accompanied by the evolution of heat and light. Combustion of a hydrocarbon in the presence of excess oxygen gives mostly CO_2 and H_2O. When the supply of oxygen is limited, mainly CO also forms, and in a very limited supply of oxygen the products are H_2O and very finely divided, mostly elemental carbon (as soot or lampblack). When hydrocarbons are burned in air, a mixture of CO_2, CO, and C are formed. The combustion of organic compounds containing only carbon, hydrogen, and oxygen also gives the same products, CO_2 and H_2O. Most nonmetals also burn in oxygen to give molecular oxides. Sulfur burns to give SO_2, which also forms when sulfur-containing fuels burn. Nitrogen reacts with oxygen to give a variety of nitrogen oxides, including NO and NO_2.

Many metals combine with oxygen in a process often called **corrosion**, but only sometimes is the reaction rapid enough to be considered combustion. The products are metal oxides.

Redox Titrations. Potassium permanganate is often used in redox titrations because it is a powerful oxidizing agent and serves as its own indicator. In acidic solutions, the purple MnO_4^- ion is reduced to the nearly colorless Mn^{2+} ion.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so that you can select the appropriate tool when needed.

Oxidizing and reducing agents (page 215)
The substance reduced is the oxidizing agent; the substance oxidized is the reducing agent.

Assigning oxidation numbers (page 217)
The rules permit us to assign oxidation numbers to elements in compounds and ions. You use changes in oxidation numbers to identify oxidation and reduction processes. Remember that when there is a conflict between two rules, the rule with the lower number is followed and the rule with the higher number is ignored.

Oxidation and reduction reactions (page 220)
In an oxidation reaction, the substance loses electrons; in a reduction reaction, the reactant gains electrons. Oxidation and reduction reactions always occur together.

Ion–electron method for acidic solutions (page 224)
Use this method when you need to obtain a balanced net ionic equation for a redox reaction in an acidic solution. Be sure to follow the steps in the order given and do not skip steps. Also, be sure to include charges on all ions.

Ion–electron method for basic solutions (page 226)
Use this method when you need to obtain a balanced net ionic equation for a redox reaction in a basic solution.

Oxidizing and nonoxidizing acids (Table 6.2, page 229)
Refer to this table to identify oxidizing and nonoxidizing acids, which enables you to anticipate the products of reactions of metals with acids. Nonoxidizing acids will react with metals below hydrogen in Table 6.3 to give H_2 and the metal ion.

Activity series of metals (Table 6.3, page 232)
When a question deals with the possible reaction of one metal with the salt of another, refer to the activity series to determine the outcome. A metal in the table will reduce the ion of any metal above it in the table, leading to a single replacement reaction.

Hydrocarbon combustion with plentiful supply of oxygen (page 236)

$$\text{hydrocarbon} + O_2 \longrightarrow CO_2 + H_2O \qquad (\text{plentiful supply of } O_2)$$

Hydrocarbon combustion with limited supply of oxygen (page 236)

$$\text{hydrocarbon} + O_2 \longrightarrow CO + H_2O \qquad (\text{limited supply of } O_2)$$

Hydrocarbon combustion with extremely limited supply of oxygen (page 236)

$$\text{hydrocarbon} + O_2 \longrightarrow C + H_2O \qquad (\text{very limited supply of } O_2)$$

Combustion of compounds containing C, H, and O (page 237)
Complete combustion gives CO_2 and H_2O,

$$(\text{C, H, O compound}) + O_2 \longrightarrow CO_2 + H_2O \qquad (\text{complete combustion})$$

Combustion of organic compounds containing sulfur (page 237)
If an organic compound contains sulfur, SO_2 is formed in addition to CO_2 and H_2O when the compound is burned.

= *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Oxidation–Reduction

6.1 Define oxidation and reduction in terms of **(a)** electron transfer and **(b)** oxidation numbers.

6.2 Why must both oxidation and reduction occur simultaneously during a redox reaction? What is an oxidizing agent? What happens to it in a redox reaction? What is a reducing agent? What happens to it in a redox reaction?

6.3 In the compound As_4O_6, arsenic has an *oxidation number* of +3. What is the *oxidation state* of arsenic in this compound?

6.4 Are the following redox reactions? Explain.

$$2NO_2 \longrightarrow N_2O_4$$

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

6.5 If the oxidation number of nitrogen in a certain molecule changes from +3 to −2 during a reaction, is the nitrogen oxidized or reduced? How many electrons are gained (or lost) by each nitrogen atom?

Ion–Electron Method

6.6 The following equation is not balanced.

$$Ag + Fe^{2+} \longrightarrow Ag^+ + Fe$$

Why? Use the ion–electron method to balance it.

6.7 What are the net charges on the left and right sides of the following equations? Add electrons as necessary to make each of them a balanced half-reaction.

(a) $NO_3^- + 10H^+ \longrightarrow NH_4^+ + 3H_2O$

(b) $Cl_2 + 4H_2O \longrightarrow 2ClO_2^- + 8H^+$

6.8 In Question 6.7, which half-reaction represents oxidation? Which represents reduction?

Acids as Oxidizing Agents and the Activity Series

6.9 What is a *single replacement reaction*?

6.10 What is a nonoxidizing acid? Give two examples. What is the oxidizing agent in a nonoxidizing acid?

6.11 What is the strongest oxidizing agent in an aqueous solution of nitric acid?

6.12 If a metal is able to react with a solution of HCl, where must the metal stand relative to hydrogen in the activity series?

6.13 Where in the activity series do we find the best reducing agents? Where do we find the best oxidizing agents?

6.14 Which metals in Table 6.3 will not react with nonoxidizing acids?

6.15 Which metals in Table 6.3 will react with water? Write chemical equations for each of these reactions.

6.16 When manganese reacts with silver ion, is manganese oxidized or reduced? Is it an oxidizing agent or a reducing agent?

Oxygen as an Oxidizing Agent

6.17 Define combustion.

6.18 Why is "loss of electrons" described as oxidation?

6.19 What are the major products produced in the combustion of $C_{10}H_{22}$ under the following conditions **(a)** an excess of oxygen **(b)** a slightly limited oxygen supply **(c)** a very limited supply of oxygen **(d)** the compound is burned in air?

6.20 If one of the impurities in diesel fuel has the formula C_2H_6S, what products will be formed when it burns? Write a balanced chemical equation for the reaction.

6.21 Burning ammonia in an atmosphere of oxygen produces stable N_2 molecules as one of the products. What is the other product? Write the balanced chemical equation for the reaction.

6.22 What does burning sulfur in air produce? What is the limiting reactant in this reaction?

Review Problems

Oxidation–Reduction; Oxidation Numbers

6.23 Assign oxidation numbers to the atoms in the following: **(a)** S^{2-}, **(b)** SO_2, **(c)** P_4, and **(d)** PH_3.

OH **6.24** Assign oxidation numbers to the atoms in the following: **(a)** ClO_4^-, **(b)** Cl^-, **(c)** SF_6, and **(d)** $Au(NO_3)_3$.

6.25 Assign oxidation numbers to each atom in the following: **(a)** NaOCl, **(b)** $NaClO_2$, **(c)** $NaClO_3$, and **(d)** $NaClO_4$.

6.26 Assign oxidation numbers to the elements in the following: **(a)** $MnCl_2$, **(b)** MnO_4^-, **(c)** MnO_4^{2-}, and **(d)** MnO_2.

6.27 Assign oxidation numbers to the elements in the following: **(a)** PbS, **(b)** $TiCl_4$, **(c)** CsO_2, and **(d)** O_2F_2.

6.28 Assign oxidation numbers to the elements in the following: **(a)** $Sr(IO_3)_2$, **(b)** Cr_2S_3, **(c)** OF_2, and **(d)** HOF.

6.29 Titanium burns in pure nitrogen to form TiN. What are the oxidation states of titanium and nitrogen in TiN?

6.30 Zirconia, which is zirconium oxide, is used to make ceramic knives. What are the oxidation states of zirconium and oxygen in zircon?

6.31 Ozone, O_3, is one of the oxidants responsible for the haze over the Smoky Mountains. What is the oxidation number of the oxygens in ozone?

6.32 The other major oxidizing agent in the Smoky Mountains is OH. What is the oxidation number of the oxygen in OH?

6.33 When chlorine is added to drinking water to kill bacteria, some of the chlorine is changed into ions by the following equilibrium:

$$Cl_2(aq) + H_2O \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

In the forward reaction (the reaction going from left to right), which substance is oxidized and which is reduced? In the reverse reaction, which is the oxidizing agent and which is the reducing agent?

6.34 A pollutant in smog is nitrogen dioxide, NO_2. The gas has a reddish brown color and is responsible for the red-brown color associated with this type of air pollution. Nitrogen dioxide is also a contributor to acid rain because when rain passes through air contaminated with NO_2, it dissolves and undergoes the following reaction:

$$3NO_2(g) + H_2O \longrightarrow NO(g) + 2H^+(aq) + 2NO_3^-(aq)$$

In this reaction, which element is reduced and which is oxidized? Which are the oxidizing agent and the reducing agent?

6.35 For the following reactions, identify the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent.

(a) $2HNO_3 + 3H_3AsO_3 \longrightarrow 2NO + 3H_3AsO_4 + H_2O$

(b) $NaI + 3HOCl \longrightarrow NaIO_3 + 3HCl$

(c) $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$

(d) $6H_2SO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$

6.36 For the following reactions, identify the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent.

(a) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(b) $3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$

(c) $5H_2SO_4 + 4Zn \longrightarrow 4ZnSO_4 + H_2S + 4H_2O$

(d) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

Ion-Electron Method

ILW **6.37** Balance the following equations for reactions occurring in an acidic solution.

(a) $S_2O_3^{2-} + OCl^- \longrightarrow Cl^- + S_4O_6^{2-}$

(b) $NO_3^- + Cu \longrightarrow NO_2 + Cu^{2+}$

(c) $IO_3^- + H_3AsO_3 \longrightarrow I^- + H_3AsO_4$

(d) $SO_4^{2-} + Zn \longrightarrow Zn^{2+} + SO_2$

(e) $NO_3^- + Zn \longrightarrow NH_4^+ + Zn^{2+}$

(f) $Cr^{3+} + BiO_3^- \longrightarrow Cr_2O_7^{2-} + Bi^{3+}$

(g) $I_2 + OCl^- \longrightarrow IO_3^- + Cl^-$

(h) $Mn^{2+} + BiO_3^- \longrightarrow MnO_4^- + Bi^{3+}$

(i) $H_3AsO_3 + Cr_2O_7^{2-} \longrightarrow H_3AsO_4 + Cr^{3+}$

6.38 Balance the following equations for reactions occurring in an acidic solution.

(a) $Sn + NO_3^- \longrightarrow SnO_2 + NO$

(b) $PbO_2 + Cl^- \longrightarrow PbCl_2 + Cl_2$

(c) $Ag + NO_3^- \longrightarrow NO_2 + Ag^+$

(d) $Fe^{3+} + NH_3OH^+ \longrightarrow Fe^{2+} + N_2O$

(e) $HNO_2 + I^- \longrightarrow I_2 + NO$

(f) $H_2C_2O_4 + HNO_2 \longrightarrow CO_2 + NO$

(g) $HNO_2 + MnO_4^- \longrightarrow Mn^{2+} + NO_3^-$

(h) $H_3PO_2 + Cr_2O_7^{2-} \longrightarrow H_3PO_4 + Cr^{3+}$

(i) $XeF_2 + Cl^- \longrightarrow Xe + F^- + Cl_2$

6.39 Balance the equations for the following reactions occurring in a basic solution.

(a) $CrO_4^{2-} + S^{2-} \longrightarrow S + CrO_2^-$

(b) $MnO_4^- + C_2O_4^{2-} \longrightarrow CO_2 + MnO_2$

(c) $ClO_3^- + N_2H_4 \longrightarrow NO + Cl^-$

(d) $NiO_2 + Mn(OH)_2 \longrightarrow Mn_2O_3 + Ni(OH)_2$

(e) $SO_3^{2-} + MnO_4^- \longrightarrow SO_4^{2-} + MnO_2$

6.40 Balance the equations for the following reactions occurring in a basic solution.

(a) $CrO_2^- + S_2O_8^{2-} \longrightarrow CrO_4^{2-} + SO_4^{2-}$

(b) $SO_3^{2-} + CrO_4^{2-} \longrightarrow SO_4^{2-} + CrO_2^-$

(c) $O_2 + N_2H_4 \longrightarrow H_2O_2 + N_2$

(d) $Fe(OH)_2 + O_2 \longrightarrow Fe(OH)_3 + OH^-$

(e) $Au + CN^- + O_2 \longrightarrow Au(CN)_4^- + OH^-$

6.41 When very dilute nitric acid reacts with a strong reducing agent such as magnesium, the nitrate ion is reduced to ammonium ion. Write a balanced net ionic equation for the reaction.

6.42 Hydroiodic acid reduces chlorine to hydrochloric acid and iodine. Write a balanced net ionic equation for the reaction.

6.43 Laundry bleach such as Clorox is a dilute solution of sodium hypochlorite, NaOCl. Write a balanced net ionic equation for the reaction of NaOCl with $Na_2S_2O_3$. The OCl^- is reduced to chloride ion and the $S_2O_3^{2-}$ is oxidized to sulfate ion.

OH **6.44** Calcium oxalate is one of the minerals found in kidney stones. If a strong acid is added to calcium oxalate, the compound will dissolve and the oxalate ion will be changed to oxalic acid (a weak acid). Oxalate ion is a moderately strong reducing agent. Write a balanced net ionic equation for the oxidation of $H_2C_2O_4$ by $K_2Cr_2O_7$ in an acidic solution. The reaction yields Cr^{3+} and CO_2 among the products.

6.45 Ozone, O_3, is a very powerful oxidizing agent, and in some places ozone is used to treat water to kill bacteria and make it safe to drink. One of the problems with this method of purifying water is that if there is any bromide ion in the water, it becomes oxidized to bromate ion, which has shown evidence of causing cancer in test animals. Assuming that ozone is reduced to water, write a balanced chemical equation for the reaction. (Assume an acidic solution.)

6.46 Chlorine is a good bleaching agent because it is able to oxidize substances that are colored to give colorless reaction products. It is used in the pulp and paper industry as a bleach, but after it has done its work, residual chlorine must be removed. This is accomplished using sodium thiosulfate, $Na_2S_2O_3$, which reacts with the chlorine, reducing it to chloride ion. The thiosulfate ion is changed to sulfate ion, which is easily removed by washing with water. Write a balanced chemical equation for the reaction of chlorine with thiosulfate ion, assuming an acidic solution.

Acids as Oxidizing Agents

6.47 Write balanced molecular, ionic, and net ionic equations for the reactions of the following metals with hydrochloric acid to give hydrogen plus the metal ion in solution.

(a) Manganese (gives Mn^{2+})

(b) Cadmium (gives Cd^{2+})

(c) Tin (gives Sn^{2+})

6.48 Write balanced molecular, ionic, and net ionic equations for the reaction of each of the following metals with dilute sulfuric acid.

(a) Nickel (gives Ni^{2+})

(b) Chromium (gives Cr^{3+})

(c) Aluminum (gives Al^{3+})

6.49 On the basis of the discussions in this chapter, suggest balanced chemical equations for the oxidation of metallic silver to Ag^+ ion with **(a)** dilute HNO_3 and **(b)** concentrated HNO_3.

OH **6.50** Hot, concentrated sulfuric acid is a fairly strong oxidizing agent. Write a balanced net ionic equation for the oxidation of metallic copper to copper(II) ion by hot, concentrated H_2SO_4, in which the sulfur is reduced to SO_2. Write a balanced molecular equation for the reaction.

Single Replacement Reactions and the Activity Series

6.51 Use Table 6.3 to predict the outcome of the following reactions. If no reaction occurs, write N.R. If a reaction occurs, write a balanced chemical equation for it.

(a) $Fe + Mg^{2+} \longrightarrow$

(b) $Cr + Pb^{2+} \longrightarrow$

(c) $Ag^+ + Fe \longrightarrow$

(d) $Ag + Au^{3+} \longrightarrow$

OH **6.52** Use Table 6.3 to predict the outcome of the following reactions. If no reaction occurs, write N.R. If a reaction occurs, write a balanced chemical equation for it.

(a) $Mn + Fe^{2+} \longrightarrow$

(b) $Cd + Zn^{2+} \longrightarrow$

(c) $Mg + Co^{2+} \longrightarrow$

(d) $Cr + Sn^{2+} \longrightarrow$

6.53 The following reactions occur spontaneously.

$$Pu + 3Tl^+ \longrightarrow Pu^{3+} + 3Tl$$
$$Ru + Pt^{2+} \longrightarrow Ru^{2+} + Pt$$
$$2Tl + Ru^{2+} \longrightarrow 2Tl^+ + Ru$$

List the metals Pu, Pt, and Tl in order of increasing ease of oxidation.

6.54 The following reactions occur spontaneously.

$$2Y + 3Ni^{2+} \longrightarrow 2Y^{3+} + 3Ni$$
$$2Mo + 3Ni^{2+} \longrightarrow 2Mo^{3+} + 3Ni$$
$$Y^{3+} + Mo \longrightarrow Y + Mo^{3+}$$

List the metals Y, Ni, and Mo in order of increasing ease of oxidation.

6.55 The following reaction occurs spontaneously.

$$Ru^{2+}(aq) + Cd(s) \longrightarrow Ru(s) + Cd^{2+}(aq)$$

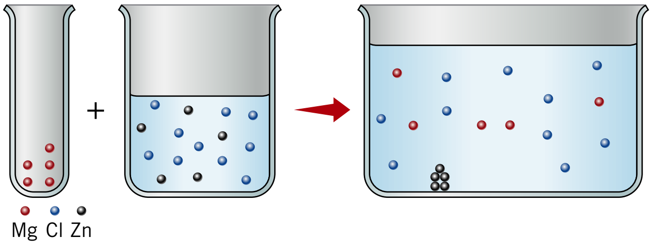
What reaction will occur if a mixture is prepared containing the following: $Cd(s)$, $Cd(NO_3)_2(aq)$, $Tl(s)$, and $TlCl(aq)$? (Refer to the information in Problem 6.53.)

6.56 When magnesium metal is dipped into a solution of nickel(II) chloride, some of the magnesium dissolves and nickel metal is deposited on the surface of the magnesium. Referring to Problem 6.54 which one of the following reactions will occur spontaneously? Explain the reason for your choice.

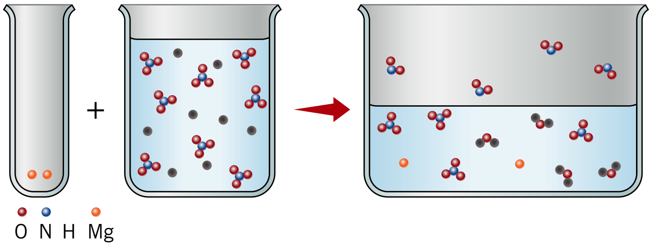
(a) $2Mo^{3+} + 3Mg \longrightarrow 3Mg^{2+} + 2Mo$

(b) $2Mo + 3Mg^{2+} \longrightarrow 2Mo^{3+} + 3Mg$

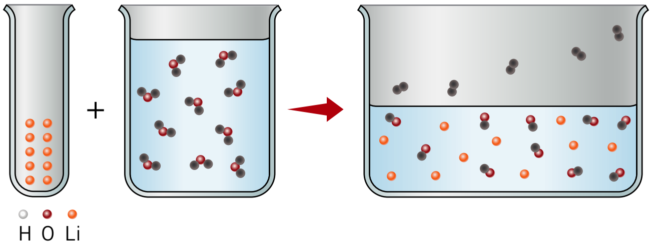
6.57 Write a balanced equation for the reaction depicted in the following visualization:



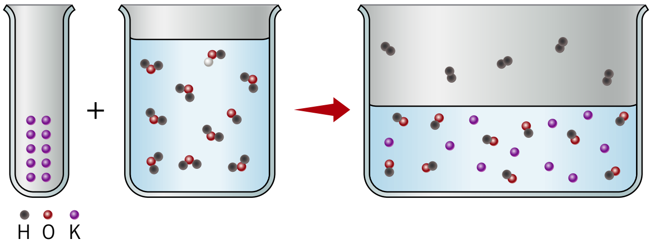
6.58 Write a balanced equation for the reaction depicted in the following visualization:



6.59 Write the balanced chemical equation for the following reaction.



6.60 Write the balanced chemical equation for the following reaction.



Reactions of Oxygen

6.61 Write balanced chemical equations for the complete combustion (in the presence of excess oxygen) of the following:

(a) C_6H_6 (benzene, an important industrial chemical and solvent)

(b) C_4H_{10} (butane, a fuel used in cigarette lighters)

(c) $C_{21}H_{44}$ (a component of paraffin wax used in candles)

6.62 Write balanced chemical equations for the complete combustion (in the presence of excess oxygen) of the following:

(a) $C_{12}H_{26}$ (a component of kerosene)

(b) $C_{18}H_{36}$ (a component of diesel fuel)

(c) C_7H_8 (toluene, a raw material in the production of the explosive TNT)

6.63 Write balanced equations for the combustion of the hydrocarbons in Problem 6.61 in **(a)** a slightly limited supply of oxygen and **(b)** a very limited supply of oxygen.

6.64 Write balanced equations for the combustion of the hydrocarbons in Problem 6.62 in **(a)** a slightly limited supply of oxygen and **(b)** a very limited supply of oxygen.

6.65 Methanol, CH_3OH, has been suggested as an alternative to gasoline as an automotive fuel. Write a balanced chemical equation for its complete combustion.

OH **6.66** The metabolism of carbohydrates such as glucose, $C_6H_{12}O_6$, produces the same products as combustion in excess oxygen. Write a chemical equation representing the metabolism (combustion) of glucose.

6.67 Write the balanced equation for the combustion of dimethylsulfide, $(CH_3)_2S$, in an abundant supply of oxygen.

6.68 Thiophene, C_4H_4S, is an impurity in crude oil and is a source of pollution if not removed. Write an equation for the combustion of thiophene.

6.69 Write chemical equations for the reaction of oxygen with **(a)** zinc, **(b)** aluminum, **(c)** magnesium, and **(d)** iron to form iron(III) oxide.

6.70 Write chemical equations for the reaction of oxygen with **(a)** beryllium, **(b)** lithium, **(c)** barium, and **(d)** bismuth to form bismuth(III) oxide.

Redox Reactions and Stoichiometry

6.71 Iodate ion reacts with sulfite ion to give sulfate ion and iodide ion.

(a) Write a balanced net ionic equation for the reaction.

(b) How many grams of sodium sulfite are needed to react with 5.00 g of sodium iodate?

6.72 Potable water (drinking water) should not have manganese concentrations in excess of 0.05 mg/mL. If the manganese concentration is greater than 0.1 mg/mL, it imparts a foul taste to the water and discolors laundry and porcelain surfaces. Manganese(II) ion is oxidized to permanganate ion by bismuthate ion, BiO_3^-, in an acidic solution. In the reaction, BiO_3^- is reduced to Bi^{3+}.

(a) Write a balanced net ionic equation for the reaction.

(b) How many milligrams of $NaBiO_3$ are needed to oxidize the manganese in 18.5 mg of manganese(II) sulfate?

OH **6.73** How many grams of copper must react to displace 12.0 g of silver from a solution of silver nitrate?

6.74 How many grams of aluminum must react to displace all of the silver from 25.0 g of silver nitrate? The reaction occurs in aqueous solution.

6.75 In an acidic solution, permanganate ion reacts with tin(II) ion to give manganese(II) ion and tin(IV) ion.

(a) Write a balanced net ionic equation for the reaction.

(b) How many milliliters of 0.230 *M* potassium permanganate solution are needed to react completely with 40.0 mL of 0.250 *M* tin(II) chloride solution?

6.76 In an acidic solution, bisulfite ion reacts with chlorate ion to give sulfate ion and chloride ion.

(a) Write a balanced net ionic equation for the reaction.

(b) How many milliliters of 0.150 *M* sodium chlorate solution are needed to react completely with 30.0 mL of 0.450 *M* sodium bisulfite solution?

6.77 Sulfites are used worldwide in the wine industry as antioxidant and antimicrobial agents. However, sulfites have also been identified as causing certain allergic reactions suffered by asthmatics, and the FDA mandates that sulfites be identified on the label if they are present at levels of 10 ppm (parts per million) or higher. The analysis of sulfites in wine uses the "Ripper method" in which a standard iodine solution, prepared by the reaction of iodate and iodide ions, is used to titrate a sample of the wine. The iodine is formed in the reaction

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

The iodine is held in solution by adding an excess of I^-, which combines with I_2 to give I_3^-. In the titration, the SO_3^{2-} is converted to SO_2 by acidification, and the reaction during the titration is

$$SO_2(aq) + I_3^-(aq) + 2H_2O \longrightarrow SO_4^{2-} + 3I^- + 4H^+$$

Starch is added to the wine sample to detect the end point, which is signaled by the formation of a dark blue color when excess iodine binds to the starch molecules. In a certain analysis, 0.0421 g of $NaIO_3$ was dissolved in dilute acid and excess NaI was added to the solution, which was then diluted to a total volume of 100.0 mL. A 50.0 mL sample of wine was then acidified and titrated with the iodine-containing solution. The volume of iodine solution required was 2.47 mL.

(a) What was the molarity of the iodine (actually, I_3^-) in the standard solution?

(b) How many grams of SO_2 were in the wine sample?

(c) If the density of the wine was 0.96 g/mL, what was the percentage of SO_2 in the wine?

(d) Parts per million (ppm) is calculated in a manner similar to percent (which is equivalent to *parts per hundred*).

$$\text{ppm} = \frac{\text{grams of component}}{\text{grams of sample}} \times 10^6 \text{ ppm}$$

What was the concentration of sulfite in the wine, expressed as parts per million SO_2?

6.78 Methylbromide, CH_3Br, is used in agriculture to fumigate soil to rid it of pests such as nematodes. It is injected directly into the soil, but over time it has a tendency to escape before it can undergo natural degradation to innocuous products. Soil chemists have found that ammonium thiosulfate, $(NH_4)_2S_2O_3$, a nitrogen and sulfur fertilizer, drastically reduces methylbromide emissions by causing it to degrade.

In a chemical analysis to determine the purity of a batch of commercial ammonium thiosulfate, a chemist first prepared a standard solution of iodine following the procedure in Problem 6.77. First, 0.462 g KIO_3 was dissolved in water to make 125 mL of solution. The solution was made acidic and treated with excess potassium iodide, which caused the following reaction to take place:

$$IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O$$

The solution containing the I_3^- ion was then diluted to exactly 250.0 mL in a volumetric flask. Next, the chemist dissolved 0.2180 g of the fertilizer in water, added starch indicator, and titrated it with the standard I_3^- solution. The reaction was

$$2S_2O_3^{2-} + I_3^- \longrightarrow S_4O_6^{2-} + 3I^-$$

The titration required 27.99 mL of the I_3^- solution.

(a) What was the molarity of the I_3^- solution used in the titration?

(b) How many grams of $(NH_4)_2S_2O_3$ were in the fertilizer sample?

(c) What was the percentage by mass of $(NH_4)_2S_2O_3$ in the fertilizer?

ILW 6.79 A sample of a copper ore with a mass of 0.4225 g was dissolved in acid. A solution of potassium iodide was added, which caused the reaction

$$2Cu^{2+}(aq) + 5I^-(aq) \longrightarrow I_3^-(aq) + 2CuI(s)$$

The I_3^- that formed reacted quantitatively with exactly 29.96 mL of 0.02100 *M* $Na_2S_2O_3$ according to the following equation.

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$$

(a) What was the percentage by mass of copper in the ore?

(b) If the ore contained $CuCO_3$, what was the percentage by mass of $CuCO_3$ in the ore?

6.80 A 1.362 g sample of an iron ore that contained Fe_3O_4 was dissolved in acid and all of the iron was reduced to Fe^{2+}. The solution was then acidified with H_2SO_4 and titrated with 39.42 mL of 0.0281 *M* $KMnO_4$, which oxidized the iron to Fe^{3+}. The net ionic equation for the reaction is

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(a) What was the percentage by mass of iron in the ore?

(b) What was the percentage by mass of Fe_3O_4 in the ore?

6.81 Hydrogen peroxide, H_2O_2, solution can be purchased in drug stores for use as an antiseptic. A sample of such a solution weighing 1.000 g was acidified with H_2SO_4 and titrated with a 0.02000 *M* solution of $KMnO_4$. The net ionic equation for the reaction is

$$6H^+ + 5H_2O_2 + 2MnO_4^- \longrightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

The titration required 17.60 mL of $KMnO_4$ solution.

(a) How many grams of H_2O_2 reacted?

(b) What is the percentage by mass of the H_2O_2 in the original antiseptic solution?

6.82 Sodium nitrite, $NaNO_2$, is used as a preservative in meat products such as frankfurters and bologna. In an acidic solution, nitrite ion is converted to nitrous acid, HNO_2, which reacts with permanganate ion according to the equation

$$H^+ + 5HNO_2 + 2MnO_4^- \longrightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$$

A 1.000 g sample of a water-soluble solid containing $NaNO_2$ was dissolved in dilute H_2SO_4 and titrated with 0.01000 *M* $KMnO_4$ solution. The titration required 12.15 mL of the $KMnO_4$ solution. What was the percentage by mass of $NaNO_2$ in the original 1.000 g sample?

6.83 A sample of a chromium-containing alloy weighing 3.450 g was dissolved in acid, and all the chromium in the sample was oxidized to CrO_4^{2-}. It was then found that 3.18 g of Na_2SO_3 was required to reduce the CrO_4^{2-} to CrO_2^- in a basic solution, with the SO_3^{2-} being oxidized to SO_4^{2-}.

(a) Write a balanced equation for the reaction of CrO_4^{2-} with SO_3^{2-} in a basic solution.

(b) How many grams of chromium were in the alloy sample?

(c) What was the percentage by mass of chromium in the alloy?

6.84 Solder is an alloy containing the metals tin and lead. A particular sample of this alloy weighing 1.50 g was dissolved in acid. All of the tin was then converted to the +2 oxidation state. Next, it was found that 0.368 g of $Na_2Cr_2O_7$ was required to oxidize the Sn^{2+} to Sn^{4+} in an acidic solution. In the reaction the chromium was reduced to Cr^{3+} ion.

(a) Write a balanced net ionic equation for the reaction between Sn^{2+} and $Cr_2O_7^{2-}$ in an acidic solution.

(b) Calculate the number of grams of tin that were in the sample of solder.

(c) What was the percentage by mass of tin in the solder?

6.85 Both calcium chloride and sodium chloride are used to melt ice and snow on roads in the winter. A certain company was marketing a mixture of these two compounds for this purpose. A chemist, wanting to analyze the mixture, dissolved 2.463 g of it in water and precipitated calcium oxalate by adding sodium oxalate, $Na_2C_2O_4$. The calcium oxalate was carefully filtered from the solution, dissolved in sulfuric acid, and titrated with 0.1000 *M* $KMnO_4$ solution. The reaction that occurred was

$$6H^+ + 5H_2C_2O_4 + 2MnO_4^- \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

The titration required 21.62 mL of the $KMnO_4$ solution.

(a) How many moles of $C_2O_4^{2-}$ were present in the calcium oxalate precipitate?

(b) How many grams of calcium chloride were in the original 2.463 g sample?

(c) What was the percentage by mass of calcium chloride in the sample?

6.86 A way to analyze a sample for nitrite ion is to acidify a solution containing NO_2^- and then allow the HNO_2 that is formed to react with iodide ion in the presence of excess I^-. The reaction is

$$2HNO_2 + 2H^+ + 3I^- \longrightarrow 2NO + 2H_2O + I_3^-$$

Then the I_3^- is titrated with $Na_2S_2O_3$ solution using starch as an indicator.

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

In a typical analysis, a 1.104 g sample that was known to contain $NaNO_2$ was treated as described above. The titration required 29.25 mL of 0.3000 *M* $Na_2S_2O_3$ solution to reach the end point.

(a) How many moles of I_3^- had been produced in the first reaction?

(b) How many moles of NO_2^- had been in the original 1.104 g sample?

(c) What was the percentage by mass of $NaNO_2$ in the original sample?

Additional Exercises

6.87 Waste water treatment often has at least one oxidation–reduction step. In the collection of waste water, chlorine can be added to control corrosion by hydrogen sulfide to give sulfur and chloride ions. What is the balanced equation for the reaction that occurs in this step?

6.88 Bromine gas is used to make fire-retardant chemicals used on children's pajamas. However, to dispose of excess bromine, it is passed through a solution of sodium hydroxide. The products are NaBr and NaOBr. What is being reduced and what is being oxidized? Write a balanced equation for the reaction.

6.89 Biodiesel is formed from the reaction of oils with methanol or ethanol. One of the products is methyl octanoate, $C_9H_{18}O_2$, which burns completely in a diesel engine. Give a balanced equation for this reaction. If the density of methyl octanoate is 0.877 g/mL, how many grams of CO_2 will be formed from the burning of 1 gallon of methyl octanoate?

6.90 What is the oxidation number of sulfur in the tetrathionate ion, $S_4O_6^{2-}$?

***6.91** In Practice Exercise 6.9 (page 221), some of the uses of chlorine dioxide were described along with a reaction that could be used to make ClO_2. Another reaction that is used to make this substance is

$$HCl + NaOCl + 2NaClO_2 \longrightarrow 2ClO_2 + 2NaCl + NaOH$$

Which element is oxidized? Which element is reduced? Which substance is the oxidizing agent and which is the reducing agent?

6.92 What is the average oxidation number of carbon in **(a)** C_2H_5OH (grain alcohol), **(b)** $C_{12}H_{22}O_{11}$ (sucrose, table sugar), **(c)** $CaCO_3$ (limestone), and **(d)** $NaHCO_3$ (baking soda)?

6.93 The following chemical reactions are *observed to occur* in aqueous solution.

$$2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$$
$$2Al + 3Fe^{2+} \longrightarrow 3Fe + 2Al^{3+}$$
$$Pb^{2+} + Fe \longrightarrow Pb + Fe^{2+}$$
$$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu$$
$$2Al + 3Pb^{2+} \longrightarrow 3Pb + 2Al^{3+}$$
$$Pb + Cu^{2+} \longrightarrow Pb^{2+} + Cu$$

Arrange the metals Al, Pb, Fe, and Cu in order of increasing ease of oxidation without referring to Table 6.3.

6.94 In Problem 6.93, were all of the experiments described actually necessary to establish the order?

6.95 According to the activity series in Table 6.3, which of the following metals react with nonoxidizing acids: **(a)** silver, **(b)** gold, **(c)** zinc, **(d)** magnesium?

6.96 In each of the following pairs, choose the metal that would most likely react more rapidly with a nonoxidizing acid such as HCl: **(a)** aluminum or iron, **(b)** zinc or nickel, and **(c)** cadmium or magnesium.

6.97 Use Table 6.3 to predict whether the following displacement reactions should occur. If no reaction occurs, write N.R. If a reaction does occur, write a balanced chemical equation for it.

(a) $Zn + Sn^{2+} \longrightarrow$
(b) $Cr + H^+ \longrightarrow$
(c) $Pb + Cd^{2+} \longrightarrow$
(d) $Zn + Co^{2+} \longrightarrow$
(e) $Mn + Pb^{2+} \longrightarrow$

6.98 Sucrose, $C_{12}H_{22}O_{11}$, is ordinary table sugar. Write a balanced chemical equation representing the metabolism of sucrose. (See Review Problem 6.66.)

***6.99** Balance the following equations by the ion–electron method.

(a) $NBr_3 \longrightarrow N_2 + Br^- + HOBr$ (basic solution)
(b) $Cl_2 \longrightarrow Cl^- + ClO_3^-$ (basic solution)
(c) $H_2SeO_3 + H_2S \longrightarrow S + Se$ (acidic solution)
(d) $MnO_2 + SO_3^{2-} \longrightarrow Mn^{2+} + S_2O_6^{2-}$ (acidic solution)
(e) $XeO_3 + I^- \longrightarrow Xe + I_2$ (acidic solution)
(f) $(CN)_2 \longrightarrow CN^- + OCN^-$ (basic solution)

6.100 Lead(IV) oxide reacts with hydrochloric acid to give chlorine. The unbalanced equation for the reaction is

$$PbO_2 + Cl^- \longrightarrow PbCl_2 + Cl_2$$

How many grams of PbO_2 must react to give 15.0 g of Cl_2?

***6.101** A solution contains $Ce(SO_4)_3^{2-}$ at a concentration of 0.0150 *M*. It was found that in a titration, 25.00 mL of this solution reacted completely with 23.44 mL of 0.032 *M* $FeSO_4$ solution. The reaction gave Fe^{3+} as a product in the solution. In this reaction, what is the final oxidation state of the Ce?

***6.102** A copper bar with a mass of 12.340 g is dipped into 255 mL of 0.125 *M* $AgNO_3$ solution. When the reaction that occurs has finally ceased, what will be the mass of unreacted copper in the bar? If all the silver that forms adheres to the copper bar, what will be the total mass of the bar after the reaction?

***6.103** A bar of copper weighing 32.00 g was dipped into 50.0 mL of 0.250 *M* $AgNO_3$ solution. If all of the silver that deposits adheres to the copper bar, how much will the bar weigh after the reaction is complete? Write and balance any necessary chemical equations.

6.104 As described in the *Chemistry Outside the Classroom 6.1*, silver tarnishes in the presence of hydrogen sulfide to form Ag_2S, which is how silver spoons tarnish. The silver can be polished and made lustrous again by placing the piece of tarnished silver in a pan with aluminum foil and detergent solution. The silver must touch the aluminum foil. Write balanced equations for both the tarnishing and the polishing of silver.

6.105 Titanium(IV) can be reduced to titanium(III) by the addition of zinc metal. Sulfur dioxide can be reduced to elemental sulfur by hydrogen. For both of these reactions, write the balanced equations. Why could we not include these compounds in the activity series table?

6.106 A researcher planned to use chlorine gas in an experiment and wished to trap excess chlorine to prevent it from escaping into the atmosphere. To accomplish this, the reaction of sodium thiosulfate ($Na_2S_2O_3$) with chlorine gas in an acidic aqueous solution to give sulfate ion and chloride ion would be used. How many grams of $Na_2S_2O_3$ are needed to trap 4.25 g of chlorine?

6.107 A sample of a tin ore weighing 0.3000 g was dissolved in an acid solution and all the tin in the sample was changed to tin(II). In a titration, 8.08 mL of 0.0500 *M* $KMnO_4$ solution was required to oxidize the tin(II) to tin(IV).

(a) What is the balanced equation for the reaction in the titration?
(b) How many grams of tin were in the sample?
(c) What was the percentage by mass of tin in the sample?
(d) If the tin in the sample had been present in the compound SnO_2, what would have been the percentage by mass of SnO_2 in the sample?

Multi-Concept Problems

6.108 In June 2002, the Department of Health and Children in Ireland began a program to distribute tablets of potassium iodate to households as part of Ireland's National Emergency Plan for Nuclear Accidents. Potassium iodate provides iodine, which when taken during a nuclear emergency, works by "topping off" the thyroid gland to prevent the uptake of radioactive iodine that might be released into the environment by a nuclear accident.

To test the potency of the tablets, a chemist dissolved one in 100.0 mL of water, made the solution acidic, and then added excess potassium iodide, which caused the following reaction to occur.

$$IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O$$

The resulting solution containing I_3^- was titrated with 0.0500 *M* $Na_2S_2O_3$ solution, using starch indicator to detect the end point. (In the presence of iodine, starch turns dark blue. When the $S_2O_3^{2-}$ has consumed all of the iodine, the solution becomes colorless.) The titration required 22.61 mL of the thiosulfate solution to reach the end point. The reaction during the titration was

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

How many milligrams of KIO_3 were in the tablet?

***6.109** An organic compound contains carbon, hydrogen, and sulfur. A sample of it with a mass of 1.045 g was burned in oxygen to give gaseous CO_2, H_2O, and SO_2. These gases were passed through 500.0 mL of an acidified 0.0200 *M* $KMnO_4$ solution, which caused the SO_2 to be oxidized to SO_4^{2-}. Only part of the available $KMnO_4$ was reduced to Mn^{2+}. Next, 50.00 mL of 0.0300 *M* $SnCl_2$ was added to a 50.00 mL portion of this solution, which still contained unreduced $KMnO_4$. There was more than enough added $SnCl_2$ to cause all of the remaining MnO_4^- in the 50 mL portion to be reduced to Mn^{2+}. The excess Sn^{2+} that still remained after the reaction was then titrated with 0.0100 *M* $KMnO_4$, requiring 27.28 mL of the $KMnO_4$ solution to reach the end point. What was the percentage of sulfur in the original sample of the organic compound that had been burned?

***6.110** A mixture is made by combining 325 mL of 0.0200 *M* $Na_2Cr_2O_7$ with 425 mL of 0.060 *M* $Fe(NO_3)_2$. Initially, the H^+ concentration in the mixture is 0.400 *M*. Dichromate ion oxidizes Fe^{2+} to Fe^{3+} and is reduced to Cr^{3+}. After the reaction in the mixture has ceased, how many milliliters of 0.0100 *M* NaOH will be required to neutralize the remaining H^+?

6.111 A solution containing 0.1244 g of $K_2C_2O_4$ was acidified, changing the $C_2O_4^{2-}$ ions to $H_2C_2O_4$. The solution was then titrated with 13.93 mL of a $KMnO_4$ solution to reach a faint pink end point. In the reaction, $H_2C_2O_4$ was oxidized to CO_2 and MnO_4^- was reduced to Mn^{2+}. What was the molarity of the $KMnO_4$ solution used in the titration?

***6.112** It was found that a 20.0 mL portion of a solution of oxalic acid, $H_2C_2O_4$, requires 6.25 mL of 0.200 *M* $K_2Cr_2O_7$ for complete reaction in an acidic solution. In the reaction, the oxidation product is CO_2 and the reduction product is Cr^{3+}. How many milliliters of 0.450 *M* NaOH are required to completely neutralize the $H_2C_2O_4$ in a separate 20.00 mL sample of the same oxalic acid solution?

***6.113** A 15.00 mL sample of a solution containing oxalic acid, $H_2C_2O_4$, was titrated with 0.02000 *M* $KMnO_4$. The titration required 18.30 mL of the $KMnO_4$ solution. If 19.69 mL of a solution of NaOH is needed to react completely with 25.00 mL of this same oxalic acid solution, what is the concentration of the NaOH solution? In the reaction, oxalate ion ($C_2O_4^{2-}$) is oxidized to CO_2 and MnO_4^- is reduced to Mn^{2+}.

***6.114** A solution with a volume of 500.0 mL contained a mixture of SO_3^{2-} and $S_2O_3^{2-}$. A 100.0 mL portion of the solution was found to react with 80.00 mL of 0.0500 *M* CrO_4^{2-} in a basic solution to give CrO_2^-. The only sulfur-containing product was SO_4^{2-}. After the reaction, the solution was treated with excess 0.200 *M* $BaCl_2$ solution, which precipitated $BaSO_4$. This solid was filtered from the solution, dried, and found to weigh 0.9336 g. Explain in detail how you can determine the molar concentrations of SO_3^{2-} and $S_2O_3^{2-}$ in the original solution.

Exercises in Critical Thinking

6.115 The ion $OSCN^-$ is found in human saliva. Discuss the problems in assigning oxidation numbers to the atoms in this ion. Suggest a reasonable set of oxidation numbers for the atoms in $OSCN^-$.

6.116 We described the ion–electron method for balancing redox equations in Section 6.2. Can you devise an alternate method using oxidation numbers?

6.117 Assuming that a chemical reaction with DNA could lead to damage causing cancer, would a very strong or a weak oxidizing agent have a better chance of being a carcinogen? Justify your answer.

6.118 Would you expect atomic oxygen and chlorine to be better or worse oxidizing agents than molecular oxygen and molecular chlorine? Justify your answer.

6.119 Do we live in an oxidizing or reducing environment? What effect might our environment have on chemistry we do in the laboratory? What effect might the environment have on the nature of the chemicals (minerals, etc.) we find on earth?

6.120 Antioxidants are touted as helping people live longer. What are antioxidants? What role do they play in longevity? In terms of this chapter, how else could antioxidants be defined? What from this chapter would make a good antioxidant?

7

Energy and Chemical Change

Chapter Outline

7.1 | Energy: The Ability to Do Work

7.2 | Internal Energy

7.3 | Measuring Heat

7.4 | Energy of Chemical Reactions

7.5 | Heat, Work, and the First Law of Thermodynamics

7.6 | Heats of Reaction

7.7 | Thermochemical Equations

7.8 | Hess's Law

7.9 | Standard Heats of Reaction

Sports drinks are often consumed to give an athlete energy during a workout or competition. The labels of these drinks list the amount of energy the sports drink provides. But how is this value measured and how can we use this energy? In this chapter we will address these questions and learn how we can get this useful energy out of chemical reactions. MLS via Getty Images, Inc.

This Chapter in Context

Energy is a term we often see in the news. We hear reports on the cost of energy and what's happening to the world's energy supplies. One might come away with the notion that energy is something you can hold in your hands and place in a bottle. Energy is not like matter, however. Instead, it is something that matter can possess—something that enables objects to move or cause other objects to move.

Nearly every chemical and physical change is accompanied by a *change* in energy. The energy changes associated with the evaporation and condensation of water drive global weather systems. The combustion of fuels produces energy changes we use to power cars and generate electricity, and our bodies use energy released in the metabolism of foods to drive biochemical processes. In this chapter we study **thermochemistry**, the branch of chemistry that deals specifically with the energy absorbed or released by chemical reactions. Thermochemistry has many practical applications, but it is also of great theoretical importance, because it provides an important link between laboratory measurements (such as temperature changes) and events on the molecular level that occur when molecules form or break apart.

Thermochemistry is part of the science of **thermodynamics**, the study of energy transfer and energy transformation. Thermodynamics allows scientists to predict whether a proposed physical change or chemical reaction can occur under a given set of conditions. It is an essential part of chemistry (and all of the natural sciences). We'll continue our study of thermodynamics in Chapter 19.

7.1 | Energy: The Ability to Do Work

■ Work is a result of a force causing an object to move. A moving car has energy because it can move another car in a collision.

As mentioned in the preceding introduction, energy is intangible; you can't hold it in your hand to study it and you can't put it in a bottle. **Energy** is something an object has if the object is able to do work. It can be possessed by the object in two different ways, as kinetic energy and as potential energy.

Kinetic energy (KE) is the energy an object has when it is moving. It depends on the object's mass and velocity; the larger the object's mass and the greater its velocity, the more kinetic energy it has. The equation that relates kinetic energy (KE) to these quantities is:

TOOLS

Kinetic energy

$$\mathrm{KE} = \frac{1}{2}mv^2 \tag{7.1}$$

where m is the mass and v is the velocity.

■ Unlike kinetic energy, there is no single, simple equation that can be used to calculate the amount of potential energy an object has.

Potential energy (PE) is energy an object has that can be changed to kinetic energy; it can be thought of as **stored energy**. For example, when you wind an alarm clock, you transfer energy to a spring. The spring holds this stored energy (potential energy) and gradually releases it, in the form of kinetic energy, to make the clock's mechanism work.

Chemicals also possess potential energy, which is sometimes called **chemical energy**. When chemical reactions occur, the changes in chemical energy possessed by the substances lead to either an absorption or a release of energy (as heat or light, for instance). For example, the explosive reaction between hydrogen and oxygen in the main engines of the space shuttle, shown in Figure 7.1, produces light, heat, and the expanding gases that help lift the vehicle from its launch pad.

Potential Energy

An important aspect of potential energy is the way it depends on the positions of objects that experience attractions or repulsions toward other objects. For example, a book has potential energy because it experiences a gravitational attraction toward the earth. Lifting the book, which changes its position, increases the potential energy. This energy is supplied by the person doing the lifting. Letting the book fall allows the potential energy to decrease. The lost potential energy is changed to kinetic energy as the book gains speed during its descent.

How potential energy varies with position for objects that attract or repel each other can be illustrated by magnets depicted in Figure 7.2. When the magnets are held in a certain way, the end of one magnet repels the end of another; we say the "north pole" of one repels the "north pole" of the other. Because the repulsions push the magnets apart, we have to do some work to move them closer together. This causes their potential energy to increase; the energy we expended pushing them together is now stored by the magnets. If we release them, they will push each other apart, and this "push" could also be made to do work for us. Likewise, if we turn one magnet around, the ends of the two magnets will attract each other—that is, the "south pole" of one magnet attracts the "north pole" of the other. Now, to pull the magnets apart, we have to do work, and this will increase their potential energy.

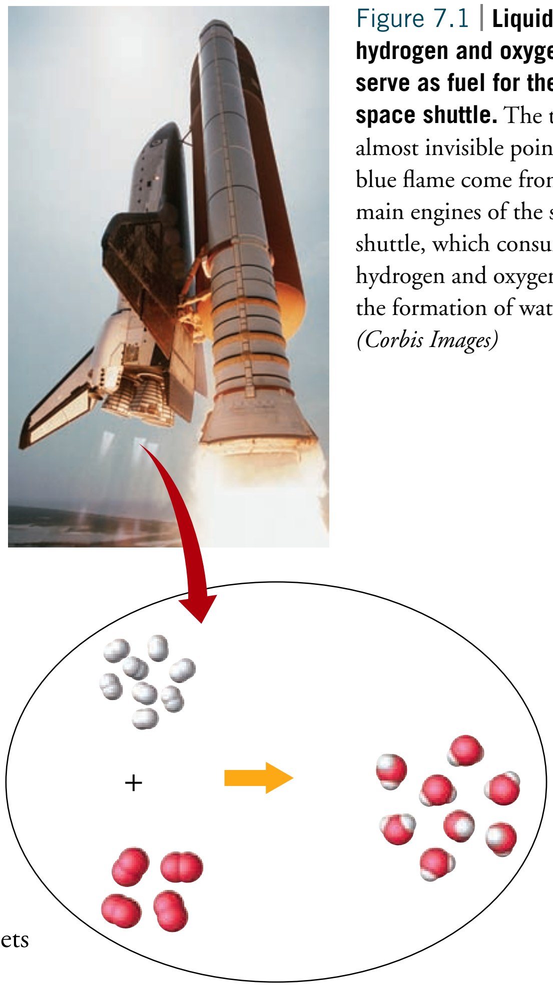


Figure 7.1 | **Liquid hydrogen and oxygen serve as fuel for the space shuttle.** The three almost invisible points of blue flame come from the main engines of the space shuttle, which consume hydrogen and oxygen in the formation of water. *(Corbis Images)*

Factors That Affect Potential Energy

- Potential energy increases when objects that attract each other move apart, and decreases when they move toward each other.
- Potential energy increases when objects that repel each other move toward each other, and decreases when they move apart.

TOOLS

Potential energy changes

If you ever have trouble remembering this, think back to the magnets and how the poles attract or repel each other.

In chemical systems, the amount of chemical energy is determined by the type and arrangement of the atoms. There aren't north and south poles, but there are attractions and repulsions between electrical charges. The attraction between opposite charges is

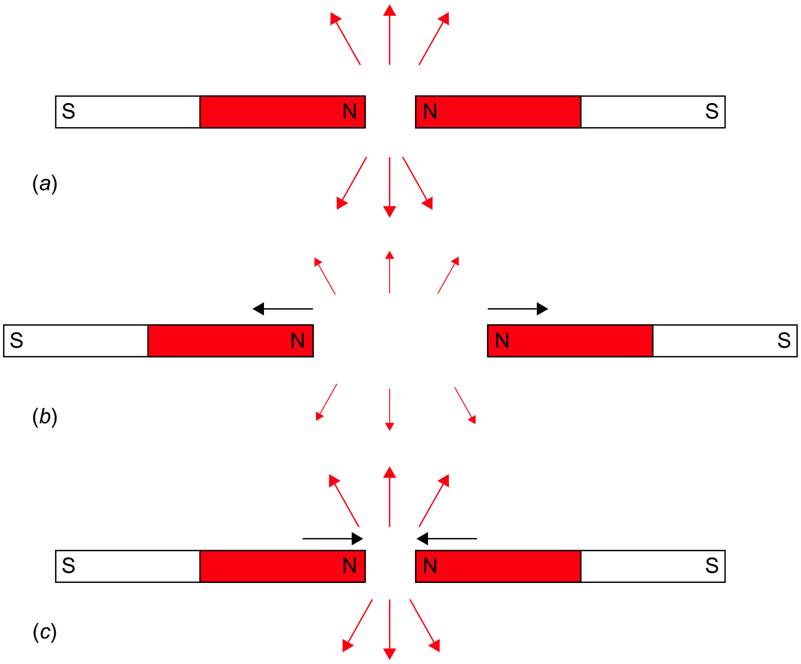
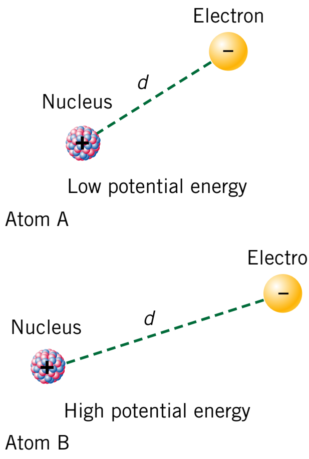


Figure 7.2 | **The potential energy of two magnets with the same poles facing depends on their distance apart.** The red arrows represent the amount of repulsion between the two magnets. (*a*) The north poles of two magnets repel when placed near each other. (*b*) When the magnets are moved apart, their potential energy decreases. (*c*) When they are moved together, their potential energy increases. *(Corbis Images)*



The positively charged nucleus attracts the negatively charged electron. As the electron is brought closer to the nucleus, the potential energy of the electron decreases. It takes work to separate the electron and the nucleus, so the electron in atom B has more potential energy than the electron in atom A.

similar to the attraction between two magnets in which the opposite poles are next to each other. Electrons are attracted to protons because of their opposite electrical charges. Electrons repel electrons and nuclei repel other nuclei because they have the same kind of electrical charge. Changes in the relative positions of these particles, as atoms join to form molecules or break apart when molecules decompose, leads to changes in potential energy. These are the kinds of potential energy changes that lead to the release or absorption of energy by chemical systems during chemical reactions.

Law of Conservation of Energy

One of the most important facts about energy is that *it cannot be created or destroyed; it can only be changed from one form to another.* This fact was established by many experiments and observations, and is known today as the **law of conservation of energy**. (Recall that when scientists say that something is "conserved," they mean that it is unchanged or remains constant.) You observe this law whenever you toss something—a ball, for instance—into the air. You give the ball some initial amount of kinetic energy when you throw it. As it rises, its potential energy increases. Because energy cannot come from nothing, the rise in potential energy comes at the expense of the ball's kinetic energy. Therefore, the ball's $\frac{1}{2}mv^2$ becomes smaller. Because the mass of the ball cannot change, the velocity (v) becomes less and the ball slows down. When all of the kinetic energy has changed to potential energy, the ball can go no higher; it has stopped moving and its potential energy is at a maximum. The ball then begins to fall, and its potential energy is changed back into kinetic energy.

Heat and Temperature

If we think about the molecular level, atoms, molecules, or ions are constantly moving and colliding with each other, which means that any object, even if we cannot see it moving, will have some kinetic energy. To get an idea of the average kinetic energy of the particles, we can measure its temperature, since the *temperature of an object is proportional to the **average** kinetic energy of its particles. The higher the average kinetic energy is, the higher the temperature.* What this means is that when the temperature of an object is raised, the molecules move faster, giving rise to more collisions with the thermometer. (Recall that KE = $\frac{1}{2}mv^2$. Increasing the average kinetic energy doesn't increase the masses of the atoms, so it must increase their speeds.) Likewise, when the temperature is reduced, the particles move slower and the average kinetic energy of the molecules is lower, so the number of collisions and the force of the collisions of the particles is lower.

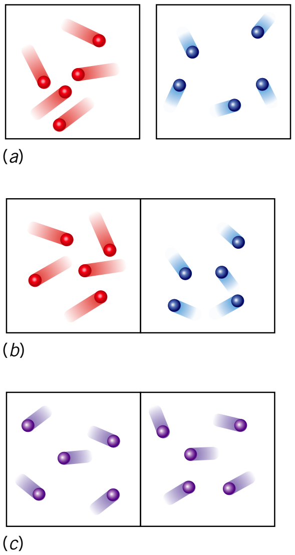


Figure 7.3 | **Energy transfer from a warmer to a cooler object.** (*a*) The longer trails on the left denote higher kinetic energies of a hot object like hot water just before it's poured into a cooler coffee cup, indicated with shorter arrows. (*b*) Collisions between the hot water molecules and the cooler molecules in the cup's material cause the water molecules to slow down and the cup's molecules to speed up, as kinetic energy is transferred from the water to the cup. (*c*) Thermal equilibrium is established: the temperatures of the water and the cup wall are now equal.

Heat is the kinetic energy (also called **thermal energy**) that is transferred on the molecular level between objects caused by differences in their temperatures. As you know, heat always passes spontaneously from a warmer object to a cooler one. This energy transfer continues until both objects come to the same temperature. Whereas heat is the amount of energy that is transferred, the temperature is proportional to the average kinetic energy of the object.

On the molecular level, when a hot object is placed in contact with a cold one, the faster atoms of the hot object collide with and lose some kinetic energy to the slower atoms of the cold object (Figure 7.3). This decreases the average kinetic energy of the particles of the hot object, causing its temperature to drop. At the same time, the average kinetic energy of the particles in the cold object is raised, causing the temperature of the cold object to rise. Eventually, the average kinetic energies of the atoms in both objects become the same and the objects reach the same temperature. Thus, the transfer of heat is interpreted as a transfer of kinetic energy between two objects.

The Joule

The SI unit of energy is a derived unit called the **joule** (symbol **J**) and corresponds to the amount of kinetic energy possessed by a 2 kilogram object moving at a speed of 1 meter per second. Using the equation for kinetic energy, KE $= \frac{1}{2}mv^2$,

$$1\ \text{J} = \frac{1}{2}\ (2\ \text{kg})\left(\frac{1\ \text{m}}{1\ \text{s}}\right)^2$$

$$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$$

The joule is actually a rather small amount of energy and in most cases we will use the larger unit, the **kilojoule (kJ)**; $1\ \text{kJ} = 1000\ \text{J} = 10^3\ \text{J}$.

Another energy unit you may be familiar with is called the **calorie (cal)**. Originally, it was defined as the energy needed to raise the temperature of 1 gram of water by 1 degree Celsius. With the introduction of the SI, the calorie has been redefined as follows:

$$1\ \text{cal} = 4.184\ \text{J} \quad \text{(exactly)} \tag{7.2}$$

The larger unit **kilocalorie (kcal)**, which equals 1000 calories, can also be related to the kilojoule:

$$1\ \text{kcal} = 4.184\ \text{kJ}$$

The nutritional or dietary Calorie (note the capital), Cal, is actually one kilocalorie.

$$1\ \text{Cal} = 1\ \text{kcal} = 4.184\ \text{kJ}$$

While joules and kilojoules are the standard units of energy, calories and kilocalories are still in common use, so you will need to be able to convert joules into calories and vice versa.

7.2 | Internal Energy

In Section 7.1 we introduced *heat* as a transfer of energy that occurs between objects with different temperatures. For example, heat will flow from a hot cup of coffee into the cooler surroundings. Eventually the coffee and surroundings come to the same temperature and we say they are in **thermal equilibrium** with each other. The temperature of the coffee has dropped and the temperature of the surroundings has increased a bit.

Energy that is transferred as heat comes from an object's internal energy. **Internal energy** is the sum of energies for all of the individual particles in a sample of matter. All of the particles within any object are in constant motion. For example, in a sample of air at room temperature, oxygen and nitrogen molecules travel faster than rifle bullets, constantly colliding with each other and with the walls of their container. The molecules spin as they move, the atoms within the molecules jiggle and vibrate, and the electrons move around the atoms; these internal molecular motions also contribute to the kinetic energy of the molecule and, thus, to the internal energy of the sample. We'll use the term **molecular kinetic energy** for the energy associated with such motions. Each particle has a certain value of molecular kinetic energy at any given moment. Molecules are continually exchanging energy with each other during collisions, but as long as the sample is isolated, the total kinetic energy of all the molecules remains constant.

■ Recall that kinetic energy is the energy of motion and is given by KE $= 1/2\ mv^2$, where m is the mass of an object and v is its velocity.

Internal energy is often given the symbol E.[1] In studying both chemical and physical changes, we will be interested in the *change* in internal energy that accompanies the process. This is defined as ΔE, where the symbol Δ (Greek letter delta) signifies a change.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

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[1] Sometimes the symbol U is used for internal energy.

For a chemical reaction, E_{final} corresponds to the internal energy of the products, so we'll write it as E_{products}. Similarly, we'll use the symbol $E_{\text{reactants}}$ for E_{initial}. So for a chemical reaction the change in internal energy is given by

$$\Delta E = E_{\text{products}} - E_{\text{reactants}} \tag{7.3}$$

Notice an important convention illustrated by this equation. Namely, changes in something like temperature (Δt) or in internal energy (ΔE) are always figured by taking "final minus initial" or "products minus reactants." This means that if a system *absorbs* energy from its surroundings during a change, its final energy is greater than its initial energy and ΔE is positive. This is what happens, for example, when photosynthesis occurs or when a battery is charged. As the system (the battery) absorbs the energy, its internal energy increases and is then available for later use elsewhere.

Temperature and Average Molecular Kinetic Energy

■ Temperature is related to the average molecular kinetic energy, but it is not equal to it. Temperature is ***not*** an energy.

The idea, introduced in Section 7.1, that atoms and molecules are in constant random motion forms the basis for the **kinetic molecular theory.** It is this theory that tells us in part that *temperature* is related to the *average kinetic energy* of the atoms and molecules of an object. Be sure to keep in mind the distinction between temperature and internal energy; the two are quite different. Temperature is related to the *average* molecular kinetic energy, whereas internal energy is related to the *total* molecular kinetic energy.[2]

The concept of an *average* kinetic energy implies that there is a distribution of kinetic energies among the molecules in an object. Let's examine this further. At any particular moment, the individual particles in an object are moving at different velocities, which gives them a broad range of kinetic energies. An extremely small number of particles will be standing still, so their kinetic energies will be zero. Another small number will have very large velocities; these will have very large kinetic energies. Between these extremes there will be many molecules with intermediate amounts of kinetic energy.

The graphs in Figure 7.4 show the kinetic energy distributions among molecules in a sample at two different temperatures. The vertical axis represents the *fraction* of molecules with a given kinetic energy (i.e., the number of molecules with a given KE divided by the total number of molecules in the sample). Each curve in Figure 7.4 describes how the fraction of molecules with a given KE varies with KE.

Each curve starts out with a fraction equal to zero when KE equals zero. This is because the fraction of molecules with zero KE (corresponding to molecules that are motionless) is essentially zero, regardless of the temperature. As we move along the KE axis we find that the fraction of the molecules increases, reaches a peak, and then declines toward zero again. For very large values of KE, the fraction drops off again because very few molecules have very large velocities.

Each curve in Figure 7.4 has a characteristic peak or maximum corresponding to the most frequently experienced values for molecular KE. Because the curves are not symmetrical, the *average* values of molecular KE lie slightly to the right of the maxima. Notice that when the temperature increases (going from curve 1 to 2), the curve flattens and the maximum shifts to a higher value, as does the average molecular KE. In fact, *if we double the Kelvin temperature, the average KE also doubles, so the Kelvin temperature is directly proportional to the average KE.* The reason the curve flattens is because the area under each curve corresponds to the *sum* of all the fractions, and when all the fractions are added, they must equal one. (No matter how you cut up a pie, if you add all the fractions, you must end up with *one* pie!)

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[2] When we're looking at heat flow, the total molecular kinetic energy is the part of the internal energy we're most interested in. However, internal energy is the total energy of all the particles in the object, so molecular potential energies (from forces of attraction and repulsion that operate between and within molecules) can and do make a large contribution to the internal energy. This is especially true in liquids and solids.

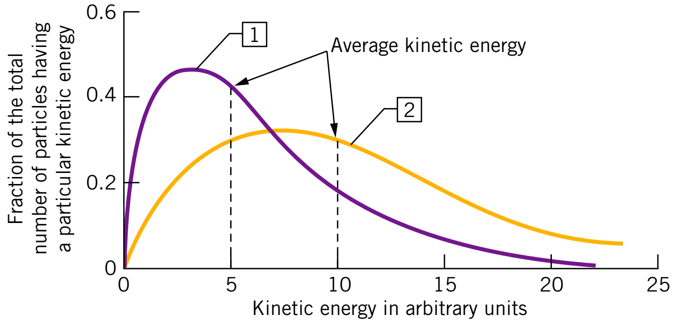


Figure 7.4 | **The distribution of kinetic energies among gas particles.** The distribution of individual kinetic energies changes in going from a lower temperature, curve 1, to a higher temperature, curve 2. The highest point on each curve is the most probable value of the kinetic energy for that temperature—that is, the one we would most frequently find if we could observe and measure the kinetic energy of each molecule. At the lower temperature, this peak is at lower values for the kinetic energy. At the higher temperature, more molecules have high speeds and fewer molecules have low speeds, so the maximum shifts to the right and the curve flattens.

We will find the graphs illustrated in Figure 7.4 very useful later when we discuss the effect of temperature on such properties as the rates of evaporation of liquids and the rates of chemical reactions.

State Functions

Equation 7.3 defines what we mean by a change in the internal energy of a chemical system during a reaction. This energy change can be made to appear entirely as heat, and as you will learn soon, we can measure heat. However, there is no way to actually measure either E_{products} or $E_{\text{reactants}}$, since this would require measuring all of the molecular motions, attractions, and repulsions. Fortunately, we are more interested in ΔE than we are in the absolute amounts of energy that the reactants or products have.

Even though we cannot measure internal energy, it is important to discuss it. As it turns out, *the energy of an object depends only on the object's current condition.* It doesn't matter how the object acquired that energy, or how it will lose it. This fact allows us to be concerned with only the change in energy, ΔE.

The *complete list of properties that specify an object's current condition* is known as the **state** of the object. In chemistry, it is usually enough to specify the object's pressure, temperature, volume, and chemical composition (numbers of moles of all substances present) to give the state of the object.

■ "State," as used in thermochemistry, doesn't have the same meaning as when it's used in terms such as "solid state" or "liquid state."

Any property, like energy, that depends *only* on an object's current state is called a **state function**. Pressure, temperature, and volume are state functions. A system's current temperature, for example, does not depend on what it was yesterday. Nor does it matter *how* the system acquired it—that is, the path to its current value. If it's now 25 °C, we know all we can or need to know about its temperature. Also, if the temperature were to increase—say, to 35 °C—the change in temperature, Δt, is simply the difference between the final and the initial temperatures:

$$\Delta t = t_{\text{final}} - t_{\text{initial}} \tag{7.4}$$

■ The symbol Δ denotes a *change between some initial and final state.*

To make the calculation of Δt, we do not have to know what caused the temperature change; all we need are the initial and final values. *This independence from the method or mechanism by which a change occurs is the important feature of all state functions.* As we'll see later, the advantage of recognizing that some property is a state function is that many calculations are then much easier.

7.3 | Measuring Heat

By measuring the amount of heat that is absorbed or released by an object, we are able to quantitatively study nearly any type of energy transfer. For example, if we want to measure the energy transferred by an electrical current, we can force the electric current through something with high electrical resistance, like the heating element in a toaster, and the energy transferred by the current becomes heat.

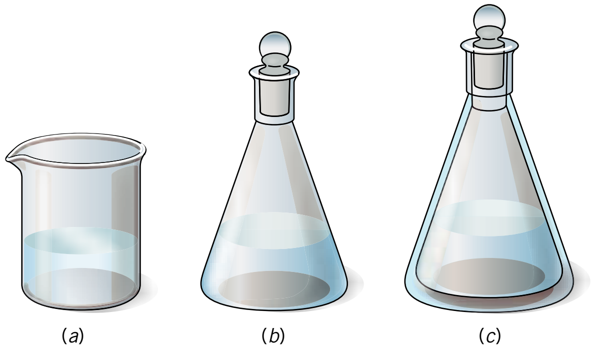

(*a*) (*b*) (*c*)

Figure 7.5 | **Open, closed, and isolated systems.** The open system (*a*) allows the exchange of both energy and mass; the closed system (*b*) only allows the exchange of energy; and the isolated system (*c*) is sealed and insulated so no heat or mass can be exchanged with the surroundings.

In our study of energy transfer, it is very important to specify the **boundary** across which the heat flows. The boundary might be visible (like the walls of a beaker) or invisible (like the boundary that separates warm air from cold air along a weather front). The boundary encloses the **system**, which is the object we are interested in studying. Everything outside the system is called the **surroundings**. The system and the surroundings together comprise the **universe**.

Three types of systems are possible, depending on whether matter or energy can cross the boundary as shown in Figure 7.5.

- **Open systems** can gain or lose mass and energy across their boundaries. The human body is an example of an open system.
- **Closed systems** can absorb or release energy, but not mass, across the boundary. The mass of a closed system is constant, no matter what happens inside. A lightbulb is an example of a closed system.
- **Isolated systems** cannot exchange matter or energy with their surroundings. Because energy cannot be created or destroyed, the energy of an isolated system is constant, no matter what happens inside. Processes that occur within an isolated system are called **adiabatic**, from the Greek *a* + *diabatos*, meaning not passable. A stoppered Thermos bottle is a good approximation of an isolated system.

The Heat and Temperature Change

TOOLS

Heat capacity

If the only type of energy that is transferred between two objects is heat energy, then all of the heat lost by one object must be gained by the second object since we have to obey the law of conservation of energy. Unfortunately, there is no instrument available that directly measures heat. Instead, we measure temperature changes, and then use them to calculate changes in heat energy. Experience tells you that the more heat you add to an object, the more its temperature will rise. In fact, experiments show that the temperature change, Δt, is *directly proportional* to the amount of heat absorbed, which we will identify by the symbol q. This can be expressed in the form of an equation as

$$q = C\,\Delta t \tag{7.5}$$

where C is a proportionality constant called the **heat capacity** of the object. The units of heat capacity are usually J °C^{-1} (or J/°C), which expresses the amount of energy needed to raise the temperature of an object by 1 °C.

Heat capacity depends on two factors. One is the size of the sample; if we double the size of the sample, we need twice as much heat to cause the same temperature increase. Heat capacity also depends on the sample's composition. For example, it's found that it takes more heat to raise the temperature of one gram of water by 1 °C than to cause the same temperature change in one gram of iron.

Specific Heat

From the preceding discussion, we see that different samples of a given substance will have different heat capacities, and this is what is observed. For example, if we have 10.0 g of water, it must absorb 41.8 J of heat energy to raise its temperature by 1.00 °C. The heat capacity of the sample is found by solving Equation 7.5 for C:

$$C = \frac{q}{\Delta t} = \frac{41.8\ \text{J}}{1.00\ \text{°C}} = 41.8\ \text{J/°C}$$

On the other hand, a 100 g sample of water must absorb 418 J of heat to have its temperature raised by 1.00 °C. The heat capacity of this sample is

$$C = \frac{q}{\Delta t} = \frac{418\ \text{J}}{1.00\ \text{°C}} = 418\ \text{J/°C}$$

Thus, a 10-fold increase in sample size has produced a 10-fold increase in the heat capacity. This indicates that the heat capacity is directly proportional to the mass of the sample.

$$C = m \times s \qquad \textbf{(7.6)}$$

where *m* is the mass of the sample and *s* is a constant called the **specific heat capacity** (or simply the **specific heat**). If the heat capacity has units of J $°C^{-1}$ and if the mass is in grams, the specific heat capacity has units of J g^{-1} $°C^{-1}$. The units tell us that the specific heat capacity is the amount of heat required to raise the temperature of 1 gram of a substance by 1 °C.

Because *C* depends on the size of the sample, *heat capacity is an extensive property*. When we discussed density in Section 2.5, you learned that if we take the ratio of two extensive properties, we can obtain an intensive property—one that is independent of the size of the sample. Because heat capacity and mass both depend on sample size, their ratio, obtained by solving Equation 7.6 for *s*, yields an intensive property that is the same for any sample of a substance.

If we substitute Equation 7.6 into Equation 7.5, we can obtain an equation for *q* in terms of specific heat.

TOOLS

Specific heat capacity

$$q = ms\,\Delta t \qquad \textbf{(7.7)}$$

We can use this equation to calculate the specific heat of water from the information given above, which states that 10.0 g of water requires 41.8 J to have its temperature raised by 1.00 °C. Solving for *s* and substituting gives

$$\begin{aligned} s &= \frac{q}{m\,\Delta t} = \frac{41.8\ \text{J}}{10.0\ \text{g} \times 1.00\ °\text{C}} \\ &= 4.18\ \text{J g}^{-1}\ °\text{C}^{-1} \end{aligned}$$

Recall that the older energy unit calorie (cal) is currently defined as 1 cal = 4.184 J. Therefore, the specific heat of water expressed in calories is

$$s = 1.000\ \text{cal g}^{-1}\ °\text{C}^{-1} \quad (\text{for } H_2O)$$

■ You should learn these values for water:

$s = 1.000$ cal g^{-1} $°C^{-1}$

$s = 4.184$ J g^{-1} $°C^{-1}$

In measuring heat, we often use an apparatus containing water, so the specific heat of water is a quantity we will use in working many problems. Every substance has its own characteristic specific heat, and some are listed in Table 7.1.

When comparing or working with mole-sized quantities of substances, we can use the **molar heat capacity,** which is the amount of heat needed to raise the temperature of 1 mol of a substance by 1 °C. Molar heat capacity equals the specific heat times the molar mass and has units of J mol^{-1} $°C^{-1}$.

Table 7.1 **Specific Heats**

Substance	Specific Heat, J g^{-1} $°C^{-1}$ (25 °C)
Carbon (graphite)	0.711
Copper	0.387
Ethyl alcohol	2.45
Gold	0.129
Granite	0.803
Iron	0.4498
Lead	0.128
Olive oil	2.0
Silver	0.235
Water (liquid)	4.184

CHEMISTRY OUTSIDE THE CLASSROOM 7.1

Water, Climate, and the Body's "Thermal Cushion"

Compared with most substances, water has a very high specific heat. A body of water can therefore gain or lose a substantial amount of heat without undergoing a large change in temperature. Because of this, the oceans of the world have a very significant moderating effect on climate. This is particularly apparent when we compare temperature extremes of locales near the oceans with those inland away from the sea and large lakes (such as the Great Lakes in the upper United States). Places near the sea tend to have cooler summers and milder winters than places located inland because the ocean serves as a thermal "cushion," absorbing heat in the summer and giving some of it back during the winter.

Warm and cool ocean currents also have global effects on climate. For example, the warm waters of the Gulf of Mexico are carried by the Gulf Stream across the Atlantic Ocean and keep winter relatively mild for Ireland, England, and Scotland. By comparison, northeastern Canada, which is at the same latitude as the British Isles, has much colder winters.

Water also serves as a thermal cushion for the human body. The adult body is about 60% water by mass, so it has a high heat capacity. In other words, the body can exchange considerable energy with the environment but experience only a small change in temperature. This makes it relatively easy for the body to maintain a steady temperature of 37 °C, which is vital to survival. With a substantial thermal cushion, the body adjusts to large and sudden changes in outside temperature while experiencing very small fluctuations of its core temperature.

Direction of Heat Flow

Heat is energy that is transferred from one object to another. This means that the heat lost by one object is the same as the heat gained by the other. To indicate the direction of heat flow, we assign a positive sign to q if the heat is gained and a negative sign if the heat is lost. For example, if a piece of warm iron is placed into a beaker of cool water and the iron loses 10.0 J of heat, the water gains 10.0 J of heat. For the iron, $q = -10.0$ J and for the water, $q = +10.0$ J.

The relationship between the algebraic signs of q in a transfer of heat can be stated in a general way by the equation

TOOLS

Heat transfer

$$q_1 = -q_2 \tag{7.8}$$

where 1 and 2 refer to the objects between which the heat is transferred.

Example 7.1

Determining the Heat Capacity of an Object

If you dry your hair with a blow drier and wear earrings at the same time, sometimes you feel the earrings get very warm—almost enough to burn your ear. Suppose that a set of earrings at 85.4 °C is dropped into an insulated coffee cup containing 25.0 g of water at 25.00 °C. The temperature of the water rises to 25.67 °C. What is the heat capacity of the earrings in J/°C?

■ **Analysis:** In this question, heat is being transferred from a warm object, the earrings, to the cooler water. We are being asked for the heat capacity, C, of the warm object. We can calculate the amount of heat gained by the water. This amount of heat is the same as the amount of heat lost by the earring. Using this amount of heat, we can then calculate the heat capacity of the earring.

■ **Assembling the Tools:** First, for the amount of heat gained by the water, q_{H_2O}, we will apply Equation 7.7 as our tool, which uses the specific heat of water (4.184 J g^{-1} °C^{-1}), the mass of water, and the temperature change for water to calculate specific heat.

Then, we can use Equation 7.8, the tool for calculating the transfer of heat from the earrings to the water, and write:

$$q_{\text{earrings}} = -q_{H_2O}$$

We have to be very careful about the algebraic signs. Because the water is gaining heat, q_{H_2O} will be a positive quantity, and because the earrings lose heat, q_{earrings} will be a negative quantity. The negative sign on the right assures us that when we substitute the positive value for q_{H_2O}, the sign of q_{earrings} will be negative.

Once we've found q_{earrings}, we will utilize Equation 7.5,

$$q = C\,\Delta t$$

the tool that relates heat capacity to temperature change and amount of heat exchanged. To find C, we divide both sides by the temperature change, Δt:

$$C = q/\Delta t$$

Solution: The temperature of the water rises from 25.00 °C to 25.67 °C, so for the water,

$$\Delta t_{H_2O} = t_{\text{final}} - t_{\text{initial}} = 25.67\ °\text{C} - 25.00\ °\text{C} = 0.67\ °\text{C}$$

The specific heat of water is $4.184\ \text{J g}^{-1}\ °\text{C}^{-1}$ and its mass is 25.0 g. Therefore, for water, the heat absorbed is

$$\begin{aligned} q_{H_2O} &= ms\,\Delta t = 25.0\ \text{g} \times 4.184\ \text{J g}^{-1}\ °\text{C}^{-1} \times 0.67\ °\text{C} \\ &= +7.0 \times 10^1\ \text{J} \end{aligned}$$

Therefore, $q_{\text{earrings}} = -7.0 \times 10^1$ J.

The temperature of the earring decreases from 85.40 °C to 25.66 °C, so

$$\Delta t_{\text{earrings}} = t_{\text{final}} - t_{\text{initial}} = 25.66\ °\text{C} - 85.40\ °\text{C} = -59.74\ °\text{C}$$

The heat capacity of the earring is then

$$C = \frac{q_{\text{earrings}}}{\Delta t_{\text{earrings}}} = \frac{-7.0 \times 10^1\ \text{J}}{-59.74\ °\text{C}} = 1.2\ \text{J/°C}$$

Is the Answer Reasonable? In any calculation involving energy transfer, we first check to see that all quantities have the correct signs. Heat capacities are positive for common objects, so the fact that we've obtained a positive value for C tells us we've handled the signs correctly.

For the transfer of a given amount of heat, the larger the heat capacity, the smaller the temperature change. The heat capacity of the water is $C = ms = 25.0\ \text{g} \times 4.18\ \text{J g}^{-1}\ °\text{C}^{-1} = 105\ \text{J}\ °\text{C}^{-1}$ and water changes temperature by 0.66 °C. The size of the temperature change for the earrings, 59.74 °C, is almost 100 times as large as that for the water, so the heat capacity should be about 1/100 that of the water. Dividing $105\ \text{J}\ °\text{C}^{-1}$ by 100 gives $1.05\ \text{J}\ °\text{C}^{-1}$, which is not too far from our answer, so our calculations seem to be reasonable.

Example 7.2

Calculating Heat from a Temperature Change, Mass, and Specific Heat

If a piece of copper wire with a mass of 20.9 g changes in temperature from 25.00 to 28.00 °C, how much heat has it absorbed?

Analysis: The question asks us to connect the heat absorbed by the wire with its temperature change, Δt. We need to know either the heat capacity of the wire or the specific heat of copper and its mass. We don't know the heat capacity of the wire. However, we do know the mass of the wire and the fact that it is made of copper, so we can look up the specific heat and calculate the amount of heat absorbed.

■ **Assembling the Tools:** We can start with Equation 7.7, the equation that relates mass, specific heat, and temperature change to the amount of heat absorbed, as our tool to solve the problem. To find the specific heat of copper, we will look at Table 7.1, which gives the specific heat of copper as 0.387 J g^{-1} $^\circ C^{-1}$.

■ **Solution:** The mass m of the wire is 20.9 g, the specific heat s is 0.387 J g^{-1} $^\circ C^{-1}$, and the temperature increases from 25.00 to 28.00 °C, so Δt is 3.00 °C. Using these values in Equation 7.7 gives

$$\begin{aligned} q &= ms\,\Delta t \\ &= (20.9\text{ g}) \times (0.387\text{ J g}^{-1}\,{}^\circ\text{C}^{-1}) \times (3.00\,{}^\circ\text{C}) \\ &= 24.3\text{ J} \end{aligned}$$

■ The sign of Δt will determine the sign of the heat exchanged. Δt is positive because ($t_{\text{final}} - t_{\text{initial}}$) is positive.

Thus, only 24.3 J raises the temperature of 20.9 g of copper by 3.00 °C. Because Δt is positive, so is q, 24.3 J. Thus, the *sign* of the energy change is in agreement with the fact that the wire *absorbs* heat.

■ **Is the Answer Reasonable?** If the wire had a mass of only 1 g and its temperature increased by 1 °C, we'd know from the specific heat of copper (let's round it to 0.39 J g^{-1} $^\circ C^{-1}$) that the ring would absorb 0.39 J. For a 3 °C increase, the answer would be three times as much, or 1.2 J. For a piece of copper a little heavier than 20 g, the heat absorbed would be 20 times as much, or about 24 J. So our answer (24.3 J) is reasonable.

Example 7.3

Calculating a Final Temperature from the Specific Heat, Heat Lost or Gained, and the Mass

If a 25.2 g piece of silver absorbs 365 J of heat, what will the final temperature of the silver be if the initial temperature is 22.2 °C? The specific heat of silver is 0.235 J g^{-1} $^\circ C^{-1}$.

■ **Analysis:** We are being asked to find the final temperature of the silver after it absorbs 365 J of heat. This question is easier to solve in two steps. First, we will manipulate Equation 7.7 to determine the change in temperature, and then we will use the initial temperature and the change in temperature to find the final temperature.

■ **Assembling the Tools:** Just as in Example 7.2, we will use Equation 7.7, $q = ms\,\Delta t$, as our tool to solve the problem. Then, we will rearrange Equation 7.4, $\Delta t = t_{\text{final}} - t_{\text{initial}}$, and use it to calculate the final temperature.

■ **Solution:** We are looking for the final temperature, so let's start by rearranging Equation 7.7 and then using the numbers.

$$q = ms\,\Delta t$$

Divide both sides by m and s:

$$\frac{q}{ms} = \frac{ms\,\Delta t}{ms}$$

Cancel out what is the same:

$$\frac{q}{ms} = \Delta t$$

The amount of heat gained is 365 J, the mass of the silver is 25.2 g, and the specific heat for silver is 0.235 J g^{-1} $^\circ C^{-1}$. Use these numbers in the equation and solve:

$$\frac{365\,\cancel{\text{J}}}{25.2\,\cancel{\text{g}} \times 0.235\,\cancel{\text{J}}\,\cancel{\text{g}}^{-1}\,{}^\circ\text{C}^{-1}} = \Delta t$$

$$\Delta t = 61.6\,{}^\circ\text{C}$$

This just gives us the change in temperature. We are really interested in the final temperature, so we will use this change of temperature and the initial temperature to determine the final temperature.

$$\begin{aligned} \Delta t &= t_{\text{final}} - t_{\text{initial}} \\ 61.6\ °\text{C} &= t_{\text{final}} - 22.2\ °\text{C} \\ t_{\text{final}} &= 61.6\ °\text{C} + 22.2\ °\text{C} \\ t_{\text{final}} &= 83.8\ °\text{C} \end{aligned}$$

■ **Is the Answer Reasonable?** Heat is being added to the system, so we would expect the temperature of the silver to increase, and it does. How much it increases depends on the amount of silver and the specific heat of silver. If we round off the numbers, we can see whether we are on the right track: the amount of heat is about 350 J, the mass is about 25 g, and the specific heat is about $0.2\ \text{J g}^{-1}\ °\text{C}^{-1}$.

$$\frac{350\ \text{J}}{25\ \text{g} \times 0.2\ \text{J g}^{-1}\ °\text{C}^{-1}} = 70\ °\text{C}$$

The change in temperature of 70 °C is very close to 61.6 °C, so it is reasonable to think that we are correct.

Practice Exercises

7.1 | A ball bearing at 220.0 °C is dropped into a cup containing 250.0 g of water at 20.0 °C. The water and ball bearing come to a temperature of 30.0 °C. What is the heat capacity of the ball bearing in J/°C? (*Hint:* How are the algebraic signs of q related for the ball bearing and the water?)

7.2 | The temperature of 255 g of water is changed from 25.0 to 30.0 °C. How much energy was transferred into the water? Calculate your answer in joules, kilojoules, calories, and kilocalories.

7.3 | Silicon, used in computer chips, has a heat capacity of $0.712\ \text{J g}^{-1}\ °\text{C}^{-1}$. If 549 J of heat is absorbed by 7.54 g of silicon, what will the final temperature be if the initial temperature is 25.0 °C?

7.4 | Energy of Chemical Reactions

Almost every chemical reaction involves the absorption or release of energy. As the reaction occurs, the potential energy (also called chemical energy) changes. To understand the origin of this energy change we need to explore the origin of potential energy in chemical systems.

In Chapter 3 we introduced you to the concept of *chemical bonds*, which are the attractive forces that bind atoms to each other in molecules, or ions to each other in ionic compounds. In this chapter you learned that since particles experience attractions or repulsions, potential energy changes occur when the particles come together or move apart. We can now bring these concepts together to understand the origin of energy changes in reactions.

Exothermic and Endothermic Reactions

Chemical reactions generally involve *both* the breaking and making of chemical bonds. In most reactions, when bonds *form*, things that attract each other move closer together, which tends to decrease the potential energy of the reacting system. When bonds *break*, on the other hand, things that are normally attracted to each other are forced apart, which increases the potential energy of the reacting system. Every reaction, therefore, has a certain net overall potential energy change, the difference between the "costs" of breaking bonds and the "profits" from making them.

In many reactions, the products have *less* potential energy (chemical energy) than the reactants. When the gas methane burns in a Bunsen burner, for example, molecules of CH_4 and O_2 with large amounts of chemical energy but relatively low amounts of molecular kinetic energy change into products (CO_2 and H_2O) that have less chemical energy but much more molecular kinetic energy. Thus, some chemical energy changes into molecular *kinetic* energy, and this increase leads to a temperature increase in the reaction mixture. If the reaction is occurring in an uninsulated system, some of this energy can be transferred to the surroundings as heat. The net result, then, is that the drop in chemical energy appears as heat that's transferred to the surroundings. In the chemical equation, therefore, we can write heat as a product.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{heat}$$

■ *exo* means "out"
endo means "in"
therm means "heat"

Any reaction in which heat is a product is said to be **exothermic.**

In some reactions the products have *more* chemical energy than the reactants. For example, green plants make energy-rich molecules of glucose ($C_6H_{12}O_6$) and oxygen from carbon dioxide and water by a multistep process called *photosynthesis.* It requires a continuous supply of energy, which is supplied by the sun. The plant's green pigment, chlorophyll, is the solar energy absorber for photosynthesis.

$$6CO_2 + 6H_2O + \text{solar energy} \xrightarrow[\text{many steps}]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$$

By an endothermic reaction, photosynthesis converts solar energy, trapped by the green pigment chlorophyll, into plant compounds that are rich in chemical energy. *(© Michele Molinari/Alamy)*

Reactions that consume energy are said to be **endothermic.** Usually such reactions change kinetic energy into potential energy (chemical energy), so the temperature of the system tends to drop as the reaction proceeds. If the reaction is occurring in an uninsulated vessel, the temperature of the surroundings will drop as heat flows into the system.

Energy of Breaking Bonds and Forming Bonds

The strength of a chemical bond is measured by how much energy is needed to break it, or by how much energy is released when the bond forms. The larger this amount of energy, the stronger the bond.

Breaking weak bonds requires relatively little energy compared to the amount of energy released when strong bonds form. This is key to understanding why burning fuels such as CH_4 produce heat. Weaker bonds between carbon and hydrogen within the fuel break so that stronger bonds in the water and carbon dioxide molecules can form, as in Figure 7.6. Burning a hydrocarbon fuel produces one molecule of carbon dioxide for each carbon atom and one molecule of water for each pair of hydrogen atoms in the fuel. Generally, the more carbon and hydrogen atoms a molecule of the fuel contains, the more strong bonds can form when it burns—and the more heat it will produce, per molecule.

We will have a lot more to say about chemical bonds and their strengths in Chapters 9 and 10.

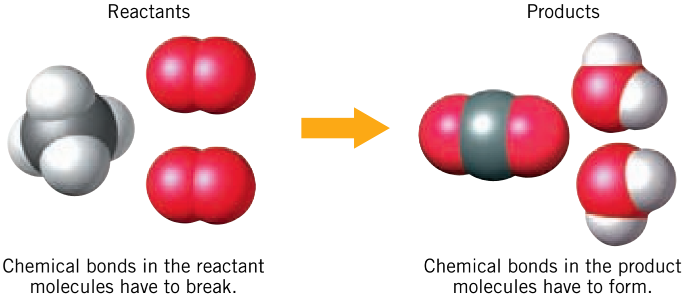

Reactants
Products
Chemical bonds in the reactant molecules have to break.
Chemical bonds in the product molecules have to form.

Figure 7.6 | **Energy changes are associated with bond breaking and bond forming.** In the combustion of methane, the C—H bonds in CH_4 molecules and the O—O bonds in O_2 molecules have to break so that the C—O bonds in CO_2 and the O—H bonds in H_2O can form. Bond breaking absorbs energy, whereas bond forming releases energy. In this reaction, more energy is released in bond formation than is absorbed in bond breaking, so overall there is a net decrease in chemical potential energy and the reaction is exothermic.

7.5 | Heat, Work, and the First Law of Thermodynamics

The amount of heat absorbed or released in a chemical reaction is called the **heat of reaction**. Heats of reaction are determined by measuring the change in temperature they cause in their surroundings, using an apparatus called a **calorimeter**. The calorimeter is often just a container with a known heat capacity in which the reaction is carried out. We can calculate the heat of reaction by measuring the temperature change the reaction causes in the calorimeter. The science of using a calorimeter for determining heats of reaction is called **calorimetry**.

■ There is no instrument that *directly* measures energy. A calorimeter does not do this; its thermometer is the only part that provides raw data, the temperature change. We *calculate* the energy change.

Calorimeter design is not standard; it varies according to the kind of reaction and the precision desired. Calorimeters are usually designed to measure heats of reaction under conditions of either constant volume or constant pressure. We have constant volume conditions if we run the reaction in a closed, rigid container. Running the reaction in an open container imposes constant-pressure conditions.

Pressure is an important variable in calorimetry, as we'll see in a moment. If you have ever blown up a balloon or worked with an auto or bicycle tire, you have already learned something about *pressure*. You know that when a tire holds air at a relatively high pressure, it is hard to dent or push in its sides because "something" is pushing back. That something is the air pressure inside the tire.

Pressure is the amount of *force* acting on a unit of area; it's the ratio of force to area:

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

You can increase the pressure in a tire by pushing or forcing air into it. Its pressure, when you stop, is whatever pressure you have added *above the initial pressure*—namely, the atmospheric pressure. We describe the air in the tire as being *compressed*, meaning that it's at a higher pressure than the atmospheric pressure.

Atmospheric pressure is the pressure exerted by the mixture of gases in our atmosphere. In English units this ratio of force to area is approximately 14.7 lb in.$^{-2}$ at sea level. The ratio does vary a bit with temperature and weather, and it varies considerably with altitude. The value of 14.7 lb in.$^{-2}$ is very close to two other common pressure units, the **standard atmosphere** (abbreviated **atm**), and the **bar**. A container that is open to the atmosphere is under a constant pressure of about 14.7 lb in.$^{-2}$, which is approximately 1 bar or 1 atm.

■ More precisely, 14.696 lb in.$^{-2}$ = 1.0000 atm = 1.0133 bar.

We've used the symbol q for heat; the symbols q_v and q_p are often used to show heats measured at constant volume or constant pressure, respectively. We must distinguish q_v from q_p. For reactions that involve big changes in volume (such as the consumption or production of a gas), the difference between the two can be significant.

Example 7.4

Computing q_v and q_p Using Calorimetry

A gas-phase chemical reaction occurs inside an apparatus similar to that shown in Figure 7.7. The reaction vessel is a cylinder topped by a piston. The piston can be locked in place with a pin. The cylinder is immersed in an insulated bucket containing a precisely weighed amount of water. A separate experiment determined that the calorimeter (which includes the piston, cylinder, bucket, and water) has a heat capacity of 8.101 kJ/°C. The reaction was run twice with identical amounts of reactants each time. The following data were collected:

Run	Pin Position	Initial Bucket Temperature (°C)	Final Bucket Temperature (°C)
1	*a* (piston locked)	24.00	28.91
2	*b* (piston unlocked)	27.32	31.54

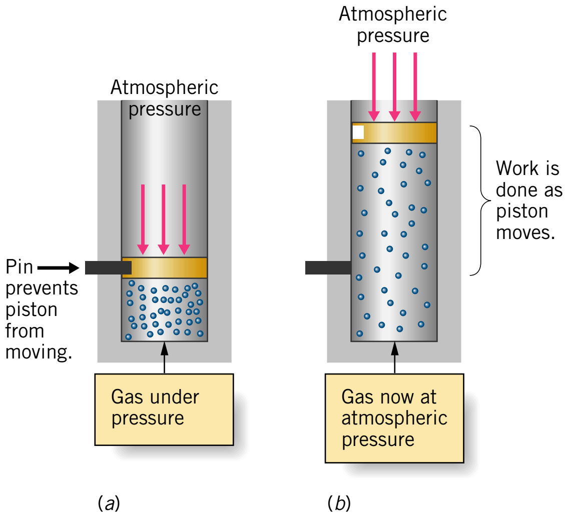

Atmospheric pressure
Pin prevents piston from moving.
Gas under pressure
(a)
Atmospheric pressure
Work is done as piston moves.
Gas now at atmospheric pressure
(b)

Figure 7.7 | **Expansion of a gas.** (*a*) A gas is confined under pressure in a cylinder fitted with a piston that is held in place by a sliding pin. (*b*) When the piston is released, the gas inside the cylinder expands and pushes the piston upward against the opposing pressure of the atmosphere. As it does so, the gas does some work on the surroundings.

Determine q_v and q_p for this reaction.

Analysis: The key to solving this problem is realizing that the heat capacity and temperature change can be used to calculate the heat absorbed by the calorimeter, which is equal in magnitude to the amount of heat lost by the reaction.

Assembling the Tools: The tools are Equation 7.5, $q = C\Delta t$, which makes it possible to measure the heat gained by the calorimeter and Equation 7.8, $q_{\text{calorimeter}} = -q_{\text{reaction}}$, which relates the heat lost by the reaction to the heat gained by the calorimeter. Run 1 will give the heat at constant volume, q_v, since the piston cannot move. Run 2 will give the heat at constant pressure, q_p, because with the piston unlocked the entire reaction will run under atmospheric pressure.

Solution: For Run 1, Equation 7.5 gives the heat absorbed by the calorimeter as

$$q = C\Delta t = (8.101 \text{ kJ/°C}) \times (28.91 \text{ °C} - 24.00 \text{ °C}) = 39.8 \text{ kJ}$$

Because the calorimeter gains heat, this amount of heat is released by the reaction, so *q for the reaction* must be negative. Therefore, $q_v = -39.8$ kJ.

For Run 2,

$$q = C\Delta t = (8.101 \text{ kJ/°C}) \times (31.54 \text{ °C} - 27.32 \text{ °C}) = 34.2 \text{ kJ}$$

so $q_p = -34.2$ kJ.

Is the Answer Reasonable? The arithmetic is straightforward, but in any calculation involving heat, always check to see that the signs of the heats in the problem make sense. The calorimeter absorbs heat, so its heats are positive. The reaction releases this heat, so its heats must be negative.

Why are q_v and q_p different for reactions that involve a significant volume change? The system in this case is the reacting mixture. If the system expands against atmospheric pressure, it is doing work. Some of the energy that would otherwise appear as heat is used up when the system pushes back the atmosphere. In Example 7.4, the work done to expand the system against atmospheric pressure is equal to the amount of "missing" heat in the constant pressure case:

$$\text{work} = (-39.8 \text{ kJ}) - (-34.2 \text{ kJ}) = -5.6 \text{ kJ}$$

The minus sign indicates that energy is leaving the system. This is called **expansion work** (or more precisely, **pressure–volume work**). A common example of pressure–volume work is the work done by the expanding gases in a cylinder of a car engine as it moves a piston.

Another example is the work done by expanding gases to lift a rocket from the ground. The amount of expansion work w done can be computed from atmospheric pressure and the volume change that the system undergoes:[3]

$$w = -P\Delta V \tag{7.9}$$

P is the *opposing pressure* against which the piston pushes, and ΔV is the change in the volume of the system (the gas) during the expansion, that is, $\Delta V = V_{\text{final}} - V_{\text{initial}}$. Because V_{final} is greater than V_{initial}, ΔV must be positive. This makes the expansion work negative.

■ The sign of w confirms that the system loses energy by doing work pushing back the atmosphere.

First Law of Thermodynamics

In chemistry, *a minus sign on an energy transfer always means that the system loses energy.* Consider what happens whenever work can be done or heat can flow in the system shown in Figure 7.7*b*. If work is negative (as in an expansion) the system loses energy and the surroundings gain it. We say work is done *by* the system. If heat is negative (as in an exothermic reaction) the system loses energy and the surroundings gain it. Either event should cause a drop in internal energy. On the other hand, if work is positive (as in a compression), the system gains energy and the surroundings lose it. We say that work is done *on* the system. If heat is positive (as in an endothermic reaction), again, the system will gain energy and the surroundings will lose it. Either positive work or positive heat should cause a positive change in internal energy.

Work and heat are simply alternative ways to transfer energy. Using this sign convention, we can relate the work w and the heat q that go into the system to the internal energy change (ΔE) the system undergoes:

$$\Delta E = q + w \tag{7.10}$$

TOOLS

First law of thermodynamics

In Section 7.2 we pointed out that the internal energy depends only on the current state of the system; we said that *internal energy, E, is a state function.* This statement (together with Equation 7.10, which is a definition of internal energy change) is a statement of the **first law of thermodynamics**. The first law implies that we can move energy around in various ways, but we cannot create energy or destroy it.

ΔE is independent of how a change takes place; it depends only on the state of the system at the beginning and the end of the change. The values of q and w depend, however, on what happens *between* the initial and final states. Thus, neither q nor w is a state function. Their values depend on the *path* of the change. For example, consider the discharge of an automobile battery by two different paths (see Figure 7.8). Both paths take us between the same two states, one being the fully charged state and the other the fully discharged state. Because E is a state function and because both paths have the same initial and final states, ΔE *must be the same for both paths.* But how about q and w?

---

[3] $P\Delta V$ must have units of energy if it is referred to as work. Work is accomplished when an opposing force, F, is pushed through some distance or length, L. The amount of work done is equal to the strength of the opposing force multiplied by the distance the force is moved:

$$\text{Work} = F \times L$$

Because pressure is force (F) per unit area, and area is simply length squared, L^2, we can write the following equation for pressure.

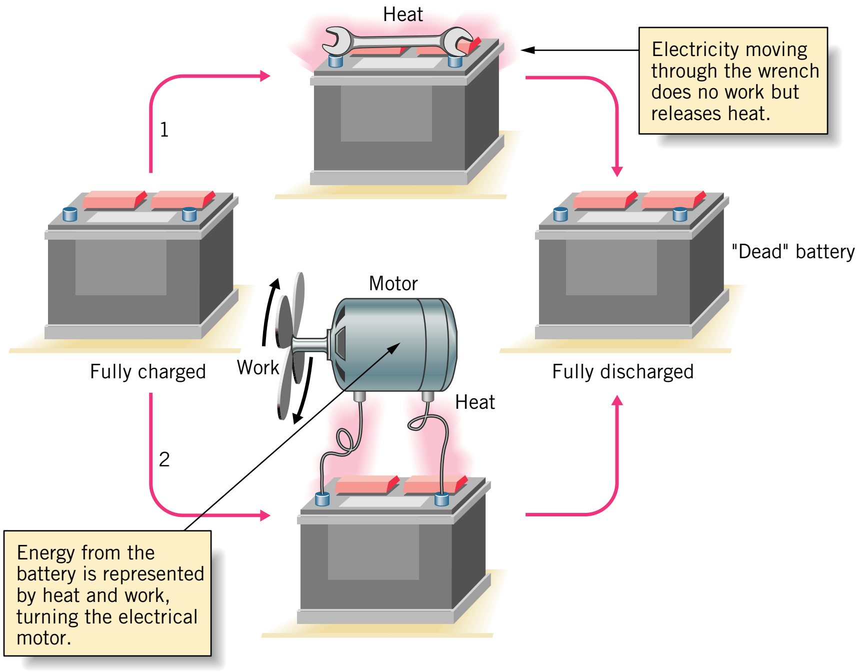
$$P = \frac{F}{L^2}$$

Volume (or a volume change) has dimensions of length cubed, L^3, so pressure times the volume change is

$$P\,\Delta V = \frac{F}{L^2} \times L^3 = F \times L$$

but, as explained previously, $F \times L$ also equals work.

Figure 7.8 | **Energy, heat, and work.** The complete discharge of a battery along two different paths yields the same total amount of energy, ΔE. However, if the battery is simply shorted with a heavy wrench, as shown in path 1, this energy appears entirely as heat. Path 2 gives part of the total energy as heat, but much of the energy appears as work done by the motor.


Heat
Electricity moving through the wrench does no work but releases heat.
1
"Dead" battery
Motor
Fully charged
Work
Fully discharged
Heat
2
Energy from the battery is represented by heat and work, turning the electrical motor.

In path 1, we simply short the battery by placing a heavy wrench across the terminals. Sparks fly and the wrench becomes very hot as the battery quickly discharges. Heat is given off, but *the system does no work* ($w = 0$). All of ΔE appears as heat.

In path 2, we discharge the battery more slowly by using it to operate a motor. Along this path, much of the energy represented by ΔE appears as work (running the motor) and only a relatively small amount appears as heat (from the friction within the motor and the electrical resistance of the wires).

There are two vital lessons here. The first is that neither q nor w is a state function. Their values depend *entirely* on the path between the initial and final states. The second lesson is that the sum of q and w, ΔE, is the same regardless of the path taken, as long as we start and stop at the same places.

7.6 | Heats of Reaction

As we have shown in Section 7.5, the change of energy in a system can be determined by measuring the amount of heat and work that is exchanged in a system. Since the amount of work that is either done by a system or on a system depends on both pressure and volume, the heat of a reaction is measured under conditions of either constant volume or constant pressure.

ΔE, Constant-Volume Calorimetry

The heats of specific reactions are sometimes given labels, for example, the heat produced by a combustion reaction is called the **heat of combustion**. Because combustion reactions require oxygen and produce gaseous products, we have to measure heats of combustion in a sealed container. Figure 7.9 shows the apparatus that is usually used to determine heats of combustion. The instrument is called a *bomb calorimeter* because the vessel holding the reaction itself resembles a small bomb. The "bomb" has rigid walls, so the change in volume, ΔV, is zero when the reaction occurs. This means, of course, that $P\Delta V$ must also be zero, and no expansion work is done, so w in Equation 7.10 is zero. Therefore, the heat of reaction measured in a bomb calorimeter is the **heat of reaction at constant volume, q_v,** and corresponds to ΔE.

$$\Delta E = q_v$$

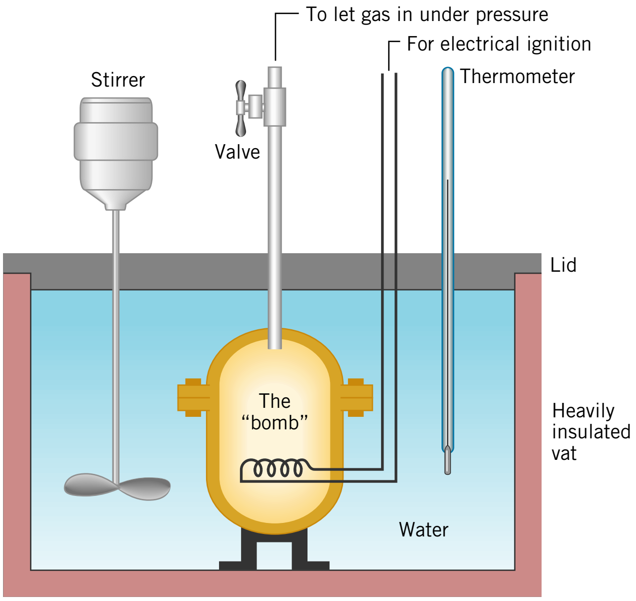


Figure 7.9 | **A bomb calorimeter.** The water bath is usually equipped with devices for adding or removing heat from the water, thus keeping its temperature constant up to the moment when the reaction occurs in the bomb. The reaction chamber is of fixed volume, so $P\Delta V$ must equal zero for reactions in this apparatus.

Food scientists determine dietary calories in foods and food ingredients by burning them in a bomb calorimeter. The reactions that break down foods in the body are complex, but they have the same initial and final states as the combustion reaction for the food.

Example 7.5
Bomb Calorimetry

(a) When 1.000 g of olive oil was completely burned in pure oxygen in a bomb calorimeter like the one shown in Figure 7.9, the temperature of the water bath increased from 22.000 °C to 26.049 °C. How many dietary Calories are in olive oil, per gram? The heat capacity of the calorimeter is 9.032 kJ/°C. (b) Olive oil is almost pure glyceryl trioleate, $C_{57}H_{104}O_6$. The equation for its combustion is

$$C_{57}H_{104}O_6\,(l) + 80O_2(g) \longrightarrow 57CO_2(g) + 52H_2O(l)$$

What is the change in internal energy, ΔE, for the combustion of one mole of glyceryl trioleate? Assume the olive oil burned in part (a) was pure glyceryl trioleate.

■ **Analysis:** Bomb calorimetry measures q_v, which is equal to the internal energy change for the reaction. In part (a), the question is asking for the amount of heat released in the combustion reaction of olive oil. All of the heat released by the reaction is absorbed by the calorimeter. By calculating the heat absorbed by the calorimeter we will be able to then calculate the amount of heat released by the reaction. Also, since only one gram was burned, the amount of heat will be per gram.

For part (b), the question is asking for the change in energy released when one mole of glyceryl trioleate is burned. We can use the information from part (a) in which we calculated the change in energy for 1 g of the substance and the molar mass of the substance to calculate the ΔE for one mole of glyceryl trioleate.

■ **Assembling the Tools:** In part (a), Equation 7.5, $q_{\text{calorimeter}} = C\,\Delta t$, is the tool to compute the heat absorbed by the calorimeter from its temperature change and heat capacity. Then we use the tool for heat transfer, $q_{\text{calorimeter}} = -q_{\text{reaction}}$, and we place a minus sign in front of the result to get the heat released by the combustion reaction.

Since the heat capacity is in kJ, the heat released will be in kJ, too. We'll need to convert kJ to dietary Calories, which are actually kilocalories (kcal). We can use the relationship

$$1 \text{ kcal} \Leftrightarrow 4.184 \text{ kJ}$$

Part (b) asks for the change in internal energy, ΔE, per mole. The heat calculated in part (a) is equal to ΔE for the combustion of 1.000 g of glyceryl trioleate. The molar mass of glyceryl trioleate is the tool to convert ΔE per gram to ΔE per mole.

■ **Solution:** First, we compute the heat absorbed by the calorimeter when 1.000 g of olive oil is burned, using Equation 7.5:

$$q_{\text{calorimeter}} = C\,\Delta t = (9.032\text{ kJ/°C}) \times (26.049\text{ °C} - 22.000\text{ °C}) = 36.57\text{ kJ}$$

Changing the algebraic sign gives the heat of combustion of 1.000 g of olive oil, $q_v = -36.57$ kJ. Part (a) asks for the heat in dietary Calories. We convert to kilocalories (kcal), which are equivalent to dietary Calories (Cal):

$$\frac{-36.57\ \cancel{\text{kJ}}}{1.000\text{ g oil}} \times \frac{1\ \cancel{\text{kcal}}}{4.184\ \cancel{\text{kJ}}} \times \frac{1\text{ Cal}}{1\ \cancel{\text{kcal}}} = -8.740\text{ Cal/g oil}$$

or we can say "8.740 dietary Calories are released when one gram of olive oil is burned." For part (b), we'll convert the heat produced per gram to the heat produced per mole, using the molar mass of $C_{57}H_{104}O_6$, 885.4 g/mol:

$$\frac{-36.57\text{ kJ}}{1.000\ \cancel{\text{g C}_{57}\text{H}_{104}\text{O}_6}} \times \frac{885.4\ \cancel{\text{g C}_{57}\text{H}_{104}\text{O}_6}}{1\text{ mol C}_{57}\text{H}_{104}\text{O}_6} = -3.238 \times 10^4\ \text{kJ/mol}$$

Since this is heat at constant volume, we have $\Delta E = q_v = -3.238 \times 10^4$ kJ for combustion of 1 mol of $C_{57}H_{104}O_6$.

■ **Is the Answer Reasonable?** Always check the signs of calculated heats first in calorimetry calculations since the signs follow the heat flow. If heat is given off, the sign for q is negative, and in combustion reactions, heat is released, so the sign of q must be negative. A tablespoon of olive oil has about 100 dietary Calories (with a tablespoon being 15 mL). Even though olive oil is less dense than water, 15 mL would weigh about 15 g. Therefore, 1 g of olive oil would have about 120 Cal/15 g $\approx$ 9 Cal/g. So, it would seem reasonable that a gram of olive oil would have about 9 dietary Calories per gram.

Practice Exercises

7.4 | The heat of combustion of methyl alcohol, CH_3OH, is -715 kJ mol^{-1}. When 2.85 g of CH_3OH was burned in a bomb calorimeter, the temperature of the calorimeter changed from 24.05 °C to 29.19 °C. What is the heat capacity of the calorimeter in units of kJ/°C? (*Hint:* Which equation relates temperature change, energy, and heat capacity?)

7.5 | A 1.50 g sample of carbon is burned in a bomb calorimeter that has a heat capacity of 8.930 kJ/°C. The temperature of the water jacket rises from 20.00 °C to 25.51 °C. What is ΔE for the combustion of 1 mole of carbon?

ΔH, Constant-Pressure Calorimetry

■ Biochemical reactions also occur at constant pressure.

Most reactions that are of interest to us do not occur at constant volume. Instead, they run in open containers such as test tubes, beakers, and flasks, where they experience the constant pressure of the atmosphere, and we can measure the **heat of reaction at constant pressure, q_p.** When reactions are run under constant pressure, they may transfer energy as heat, q_p, *and* as expansion work, w, so to calculate ΔE we need Equation 7.11:

$$\Delta E = q_p + w \tag{7.11}$$

■ From the Greek *en* + *thalpein*, meaning to heat or to warm.

This is inconvenient. If we want to calculate the internal energy change for the reaction, we'll have to measure its volume change and then use Equation 7.9. To avoid this problem, scientists have defined a "corrected" internal energy called **enthalpy**, or ***H***. Enthalpy is defined by the equation

$$H = E + PV$$

At constant pressure,

$$\begin{aligned}\Delta H &= \Delta E + P\Delta V \\ &= (q_p + w) + P\Delta V\end{aligned}$$

From Equation 7.9, $P\Delta V = -w$, so

$$\begin{aligned}\Delta H &= (q_p + w) + (-w) \\ \Delta H &= q_p \qquad \textbf{(7.12)}\end{aligned}$$

Like E, H is a state function.

As with internal energy, an **enthalpy change, ΔH**, is defined by the equation

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

For a chemical reaction, this can be rewritten as follows:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \qquad \textbf{(7.13)}$$

Positive and negative values of ΔH have the same interpretation as positive and negative values of ΔE.

> Significance of the sign of ΔH:
>
> For an endothermic change, ΔH is positive.
> For an exothermic change, ΔH is negative.

TOOLS

Algebraic sign of ΔH

The difference between ΔH and ΔE for a reaction equals $P\Delta V$. This difference can be fairly large for reactions that produce or consume gases, because these reactions can have very large volume changes. For reactions that involve only solids and liquids, though, the values of ΔV are tiny, so ΔE and ΔH for these reactions are nearly identical.

■ Research-grade calorimeters have greater accuracy and precision than the coffee-cup calorimeter.

A very simple constant-pressure calorimeter, dubbed the coffee-cup calorimeter, is made of two nested and capped cups made of foamed polystyrene, a very good insulator (Figure 7.10). A reaction occurring between aqueous solutions in such a calorimeter exchanges very little heat with the surroundings, particularly if the reaction is fast. The temperature change is rapid and easily measured. We can use Equation 7.5, $q = C\,\Delta t$, to find the heat of reaction, if we have determined the heat capacity of the calorimeter and its contents. The coffee cup and the thermometer absorb only a tiny amount of heat, and we can usually ignore them in our calculations, and just assume that all of the heat from the reaction is transferred to the reaction mixture.

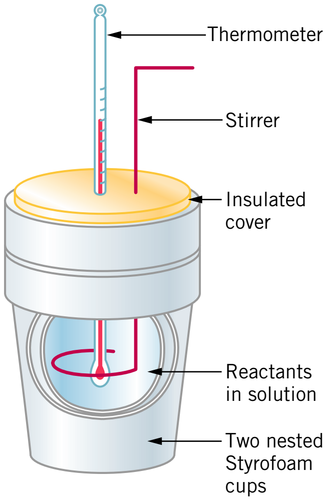


Figure 7.10 | **A coffee cup calorimeter used to measure heats of reaction at constant pressure.** Typically, aqueous solutions of the reactants, whose temperatures have been measured, are combined in the calorimeter and the temperature change of the mixture is noted as the reaction proceeds to completion. The temperature change and the heat capacities of the solutions containing the reactants are used to calculate the heat released or absorbed in the reaction.

Example 7.6
Constant-Pressure Calorimetry

The reaction of hydrochloric acid and sodium hydroxide is very rapid and exothermic. The equation is

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}$$

In one experiment, a student placed 50.0 mL of 1.00 M HCl at 25.5 °C in a coffee cup calorimeter. To this was added 50.0 mL of 1.00 M NaOH solution also at

25.5 °C. The mixture was stirred, and the temperature quickly increased to 32.2 °C. What is ΔH expressed in kJ per mole of HCl? Because the solutions are relatively dilute, we can assume that their specific heats are close to that of water, 4.184 J g^{-1} $°C^{-1}$. The density of 1.00 M HCl is 1.02 g mL^{-1} and that of 1.00 M NaOH is 1.04 g mL^{-1}. (We will neglect the heat lost to the coffee cup itself, to the thermometer, or to the surrounding air.)

■ **Analysis:** The reaction is taking place at constant pressure, so the heat we're calculating is q_p, which equals ΔH. We're given the specific heat of the solutions, so to calculate q_p we also need the system's total mass and the temperature change. The mass here refers to the *total* grams of the combined solutions. We've been given volumes, however, so we have to use their densities as a tool to calculate their masses, which you learned to do in Chapter 2.

■ **Assembling the Tools:** To calculate q_p, we will use Equation 7.7, $q = ms\,\Delta t$, as the tool to calculate the heat gained by the solution, and then Equation 7.8, $q_1 = -q_2$, which relates the heat gained by the solution to the heat released by the reaction. In order to determine the mass of the solution, we will also need to use the volume and the density tools from Chapter 2. Finally, we will need to use the tool from Chapter 5 that converts molarity to moles using volume to calculate q_p in terms of moles of HCl.

■ **Solution:** For the HCl solution, the density is 1.02 g mL^{-1} and we have

$$\text{mass (HCl)} = \frac{1.02\text{ g}}{1.00\text{ mL}} \times 50.0\text{ mL} = 51.0\text{ g}$$

Similarly, for the NaOH solution, the density is 1.04 g mL^{-1} and

$$\text{mass (NaOH)} = \frac{1.04\text{ g}}{1.00\text{ mL}} \times 50.0\text{ mL} = 52.0\text{ g}$$

The mass of the final solution is thus the sum, 103.0 g.

The reaction changes the system's temperature by $(t_{\text{final}} - t_{\text{initial}})$, so

$$\Delta t = 32.2\ °\text{C} - 25.5\ °\text{C} = 6.7\ °\text{C}$$

Now we can calculate the heat absorbed by the solution using Equation 7.7.

$$\begin{aligned}\text{Heat absorbed by the solution} &= \text{mass} \times \text{specific heat} \times \Delta t \\ &= 103.0\text{ g} \times 4.184\text{ J g}^{-1}\ °\text{C}^{-1} \times 6.7\ °\text{C} \\ &= 2.9 \times 10^3\text{ J} = 2.9\text{ kJ}\end{aligned}$$

According to the first law of thermodynamics, energy cannot be created or destroyed, so all of the heat absorbed by the solution must come from the reaction, and in which case we can write:

$$q_{\text{reaction}} = -q_{\text{solution}}$$
$$q_{\text{reaction}} = -2.9\text{ kJ}$$

However, this is q_p specifically for the mixture prepared; the problem calls for kilojoules *per mole* of HCl. The tool we use to calculate the number of moles of HCl is the molarity, which provides a conversion factor connecting volume and moles. In 50.0 mL of HCl solution (0.0500 L) we have

$$0.0500\ \cancel{\text{L HCl soln}} \times \frac{1.00\text{ mol HCl}}{1.00\ \cancel{\text{L HCl soln}}} = 0.0500\text{ mol HCl}$$

The neutralization of 0.0500 mol of acid has $q_p = -2.9$ kJ. To calculate the heat released per mole, ΔH, we simply take the ratio of joules to moles.

$$\Delta H\text{ per mole of HCl} = \frac{-2.9\text{ kJ}}{0.0500\text{ mol HCl}} = -58\text{ kJ mol}^{-1}$$

Thus, ΔH for neutralizing HCl by NaOH is −58 kJ mol^{-1} HCl.

Is the Answer Reasonable? Let's first review the logic of the steps we used. *Notice how the logic is driven by definitions, which carry specific units.* Working backward, knowing that we want units of kilojoules per mole in the answer, we must calculate separately the number of moles of acid neutralized and the number of kilojoules that evolved. The latter will emerge when we multiply the solution's mass (g) and specific heat ($J\ g^{-1}\ °C^{-1}$) by the degrees of temperature increase (°C). A simple change from joules to kilojoules is also required.

We can check the answer with some simplified arithmetic. Let's start with the mass of the solution. Because the densities are close to $1\ g\ mL^{-1}$, each solution has a mass of about 50 g, so the mixture weighs about 100 g.

The heat evolved will equal the specific heat times the mass times the temperature change. The specific heat is around $4\ J\ g^{-1}\ °C^{-1}$, the mass is about 100 g, and the temperature change is about 7 °C. The heat evolved will be approximately 4×700, or 2800 J. That's equal to 2.8×10^3 J or 2.8 kJ. Our answer of 2.9 kJ is certainly reasonable. This much heat is associated with neutralizing 0.05 mol HCl, so the heat per mole is 2.9 kJ divided by 0.05 mol, or $58\ kJ\ mol^{-1}$.

Practice Exercises

7.6 | For Example 7.6, calculate ΔH per mole of NaOH. (*Hint:* How many moles of NaOH were neutralized in the reaction?)

7.7 | When pure sulfuric acid dissolves in water, heat is given off. To measure it, 175 g of water was placed in a coffee cup calorimeter and chilled to 10.0 °C. Then 4.90 g of sulfuric acid (H_2SO_4), also at 10.0 °C, was added, and the mixture was quickly stirred with a thermometer. The temperature rose rapidly to 14.9 °C. Assume that the value of the specific heat of the solution is $4.184\ J\ g^{-1}\ °C^{-1}$, and that the solution absorbs all the heat evolved. Calculate the heat evolved in kilojoules by the formation of this solution. (Remember to use the *total* mass of the solution, the water plus the solute.) Calculate also the heat evolved *per mole* of sulfuric acid.

7.8 | Dissolving NH_4NO_3 in water is an endothermic process. In fact, this reaction is often used in cold packs sold at the drug store. When 20.0 g of NH_4NO_3 was rapidly dissolved in 75.0 mL of water in a coffee cup calorimeter, the temperature dropped from 25.7 °C to 10.4 °C. Assuming that the specific heat of the solution is $4.184\ J\ g^{-1}\ °C^{-1}$ and that the solution was isolated from the surroundings, calculate the heat absorbed by the reaction in kJ per mole of NH_4NO_3.

7.7 | Thermochemical Equations

As we have seen, the amount of heat a reaction produces or absorbs depends on the number of moles of reactants we combine. It makes sense that if we burn two moles of carbon, we're going to get twice as much heat as we would if we had burned one mole. For heats of reaction to have meaning, we must describe the **system** completely. Our description must include amounts and concentrations of reactants, amounts and concentrations of products, temperature, and pressure, because all of these things can influence heats of reaction.

Chemists have agreed to a set of **standard states** to make it easier to report and compare heats of reaction. Most thermochemical data are reported for a pressure of 1 bar, or (for substances in aqueous solution) a concentration of 1 *M*. A temperature of 25 °C (298 K) is often specified as well, although temperature is not part of the definition of standard states in thermochemistry.

- Unless we specify otherwise, whenever we write ΔH we mean ΔH for the *system*, not the surroundings.
- IUPAC recommends the use of the *bar*, instead of atmospheres, for standard states.

$\Delta H°$, Enthalpy Change for a Reaction at Standard State

The **standard heat of reaction** is the value of ΔH for a reaction occurring under standard conditions and involving the actual numbers of *moles* specified by the coefficients of the equation. To show that ΔH is for *standard* conditions, a degree sign is added to ΔH to make ΔH° (pronounced "delta H naught" or "delta H zero"). The units of ΔH° are really kilojoules/reaction.

To illustrate clearly what we mean by ΔH°, let us use the reaction between gaseous nitrogen and hydrogen that produces gaseous ammonia.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

When 1.000 mol of N_2 and 3.000 mol of H_2 react to form 2.000 mol of NH_3 at 25 °C and 1 bar, the reaction releases 92.38 kJ. Hence, for the reaction *as given by the preceding chemical equation*, $\Delta H^\circ = -92.38$ kJ. Often the enthalpy change is given immediately after the equation; for example,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ = -92.38\ \text{kJ}$$

TOOLS

Thermochemical equations

An equation that also shows the value of ΔH° is called a **thermochemical equation**. It always gives the physical states of the reactants and products, and *its ΔH° value is true only when the coefficients of the reactants and products are taken to mean moles of the corresponding substances.* The above equation, for example, shows a release of 92.38 kJ if *two* moles of NH_3 form. If we were to make twice as much or 4.000 mol of NH_3 (from 2.000 mol of N_2 and 6.000 mol of H_2), then twice as much heat (184.8 kJ) would be released. On the other hand, if only 0.5000 mol of N_2 and 1.500 mol of H_2 were to react to form 1.000 mole of NH_3, then only half as much heat (46.19 kJ) would be released. To describe the various *sizes* of the reactions just described, we write the following thermochemical equations:

$$\begin{aligned}
N_2(g) + 3H_2(g) &\longrightarrow 2NH_3(g) &\qquad \Delta H^\circ &= -92.38\ \text{kJ}\\
2N_2(g) + 6H_2(g) &\longrightarrow 4NH_3(g) &\qquad \Delta H^\circ &= -184.8\ \text{kJ}\\
\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) &\longrightarrow NH_3(g) &\qquad \Delta H^\circ &= -46.19\ \text{kJ}
\end{aligned}$$

Because the coefficients of a thermochemical equation always mean *moles*, not molecules, we may use fractional coefficients. (In the kinds of equations you've seen up till now, fractional coefficients were not allowed because we cannot have fractions of *molecules*, but we can have fractions of moles in a thermochemical equation.)

You must write down physical states for all reactants and products in thermochemical equations. The combustion of 1 mol of methane, for example, has different values of ΔH° if the water produced is in its liquid or its gaseous state.

$$\begin{aligned}
CH_4(g) + 2O_2(g) &\longrightarrow CO_2(g) + 2H_2O(l) &\qquad \Delta H^\circ &= -890.5\ \text{kJ}\\
CH_4(g) + 2O_2(g) &\longrightarrow CO_2(g) + 2H_2O(g) &\qquad \Delta H^\circ &= -802.3\ \text{kJ}
\end{aligned}$$

(The difference in ΔH° values for these two reactions is the amount of energy that would be released by the physical change of 2 mol of water vapor at 25 °C to 2 mol of liquid water at 25 °C.)

Example 7.7
Writing a Thermochemical Equation

The following thermochemical equation is for the exothermic reaction of hydrogen and oxygen that produces water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H^\circ = -571.8\ \text{kJ}$$

What is the thermochemical equation for this reaction when 1.000 mol of H_2O is produced?

■ **Analysis:** The given equation is for 2.000 mol of H_2O, and any changes in the coefficient for water must be made identically to all other coefficients, *as well as to the value of ΔH°*.

Assembling the Tools: We will use the tools for the definition of a thermochemical equation, the relationship between coefficients and ΔH, and the fact that when we change the amount of reactants, we change the amount of heat for the reaction. Since we are dividing the number of moles of water in half, we must divide the rest of the coefficients by 2 and the heat of the reaction by 2.

Solution: We divide everything by 2, to obtain

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -258.9 \text{ kJ}$$

Is the Answer Reasonable? Compare the equation just found with the initial equation to see that the coefficients and the value of ΔH° are all divided by 2.

Practice Exercises

7.9 | The combustion of methane can be represented by the following thermochemical equation:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890.5 \text{ kJ}$$

Write the thermochemical equation for the combustion of methane when 1/2 mol of $H_2O(l)$ is formed. [*Hint:* What do you have to do to the coefficient of $H_2O(l)$ to give $\tfrac{1}{2}H_2O(l)$?]

7.10 | What is the thermochemical equation for the formation of 5.000 mol of $H_2O(l)$ from $H_2(g)$ and $O_2(g)$?

7.8 | Hess's Law

Recall from Section 7.6 that enthalpy is a state function. This important fact permits us to calculate heats of reaction for reactions that we cannot actually carry out in the laboratory. You will see soon that to accomplish this, we will combine known thermochemical equations, which usually requires that we manipulate them in some way.

Manipulating Thermochemical Equations

In the last section you learned that if we change the size of a reaction by multiplying or dividing the coefficients of a thermochemical equation by some factor, the value of ΔH° is multiplied by the same factor. Another way to manipulate a thermochemical equation is to change its direction. For example, the thermochemical equation for the combustion of carbon in oxygen to give carbon dioxide is

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5 \text{ kJ}$$

The reverse reaction, which is extremely difficult to carry out, would be the decomposition of carbon dioxide to carbon and oxygen. The law of conservation of energy requires that its value of ΔH° equals +393.5 kJ.

$$CO_2(g) \longrightarrow C(s) + O_2(g) \qquad \Delta H^\circ = +393.5 \text{ kJ}$$

In effect, these two thermochemical equations tell us that the combustion of carbon is exothermic (as indicated by the negative sign of ΔH°) and that the reverse reaction is endothermic. The same amount of energy is involved in both reactions—it is just the direction of energy flow that is different. The lesson to learn here is that *we can reverse any thermochemical equation as long as we change the sign of its* ΔH°.

Enthalpy of Reactions

What we're leading up to is a method for combining known thermochemical equations in a way that will allow us to calculate an unknown $\Delta H°$ for some other reaction. Let's revisit the combustion of carbon to see how this works.

We can imagine two paths leading from 1 mol each of carbon and oxygen to 1 mol of carbon dioxide.

One-Step Path. Let C and O_2 react to give CO_2 directly.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -393.5 \text{ kJ}$$

Two-Step Path. Let C and O_2 react to give CO, and then let CO react with more O_2 to give CO_2.

Step 1. $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H° = -110.5 \text{ kJ}$

Step 2. $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -283.0 \text{ kJ}$

Overall, the two-step path consumes 1 mol each of C and O_2 to make 1 mol of CO_2, just like the one-step path. The initial and final states for the two routes to CO_2, in other words, are identical.

Because $\Delta H°$ depends only on the initial and final states and is independent of path, the values of $\Delta H°$ for both routes should be identical. We can see that this is exactly true simply by adding the equations for the two-step path and comparing the result with the equation for the single step.

$$\begin{array}{ll}
\textbf{Step 1.}\quad C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H° = -110.5 \text{ kJ} \\
\underline{\textbf{Step 2.}\quad CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)} & \Delta H° = -283.0 \text{ kJ} \\
CO(g) + C(s) + O_2(g) \longrightarrow CO_2(g) + CO(g) & \Delta H° = -110.5 \text{ kJ} + (-283.0 \text{ kJ}) \\
 & \Delta H° = -393.5 \text{ kJ}
\end{array}$$

The equation resulting from adding Steps 1 and 2 has $CO(g)$ appearing *identically* on opposite sides of the arrow. We can cancel them to obtain the net equation. *Such a cancellation is permitted only when both the formula and the physical state of a species are identical on opposite sides of the arrow.* The net thermochemical equation for the two-step process, therefore, is

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -393.5 \text{ kJ}$$

The results, chemically and thermochemically, are thus identical for both routes to CO_2.

Enthalpy Diagrams

TOOLS

Enthalpy diagram

The energy relationships among the alternative pathways for the same overall reaction can be depicted using a graphical construction called an **enthalpy diagram.** Figure 7.11 is an enthalpy diagram for the formation of CO_2 from C and O_2. The vertical axis is an energy scale for enthalpy. Each horizontal line corresponds to a certain total amount of enthalpy, which we can't actually measure, for all the substances listed on the line in the physical states specified. We *can* measure differences in enthalpy, however, and that's what we use the diagram for. Lines higher up the enthalpy scale represent larger amounts of enthalpy, so going from a lower line to a higher line corresponds to an increase in enthalpy and a positive value for $\Delta H°$ (an endothermic change). The size of $\Delta H°$ is represented by the vertical distance between the two lines. Likewise, going from a higher line to a lower one represents a decrease in enthalpy and a negative value for $\Delta H°$ (an exothermic change).

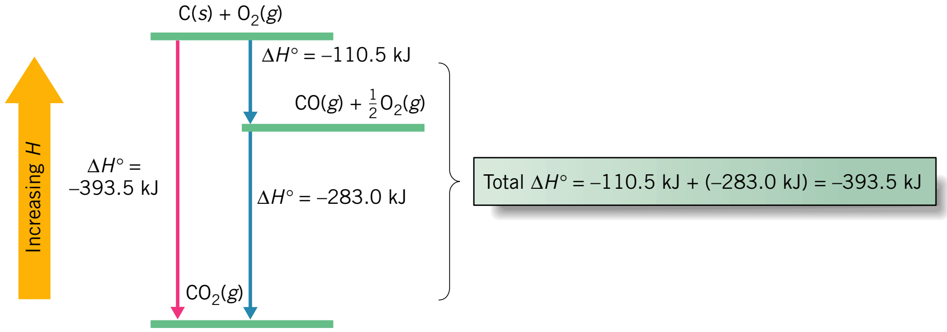


Figure 7.11 | **An enthalpy diagram for the formation of $CO_2(g)$ from its elements by two different paths.** On the left is path 1, the direct conversion of $C(s)$ and $O_2(g)$ to $CO_2(g)$. On the right, path 2 shows two shorter, downward-pointing arrows. The first step of path 2 takes the elements to $CO(g)$, and the second step takes $CO(g)$ to $CO_2(g)$. The overall enthalpy change is identical for both paths, since enthalpy is a state function.

Notice in Figure 7.11 that the line for the absolute enthalpy of $C(s) + O_2(g)$, taken as the sum, is above the line for the final product, CO_2. On the left side of Figure 7.11, we see a long downward arrow that connects the enthalpy level for the reactants, $C(s) + O_2(g)$, to that of the final product, $CO_2(g)$. This is for the one-step path, the direct path.

On the right we have the two-step path. Here, Step 1 brings us to an intermediate enthalpy level corresponding to the intermediate products, $CO(g) + \frac{1}{2}O_2(g)$. These include the mole of $CO(g)$ made in the first step plus $\frac{1}{2}$ mol of O_2 that has not reacted. Then, Step 2 occurs to give the final product. What the enthalpy diagram shows is that the total decrease in enthalpy is the same regardless of the path.

Example 7.8
Preparing an Enthalpy Diagram

Hydrogen peroxide, H_2O_2, decomposes into water and oxygen by the following equation:

$$H_2O_2(l) \longrightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

Construct an enthalpy diagram for the following two reactions of hydrogen and oxygen, and use the diagram to determine the value of $\Delta H°$ for the decomposition of hydrogen peroxide.

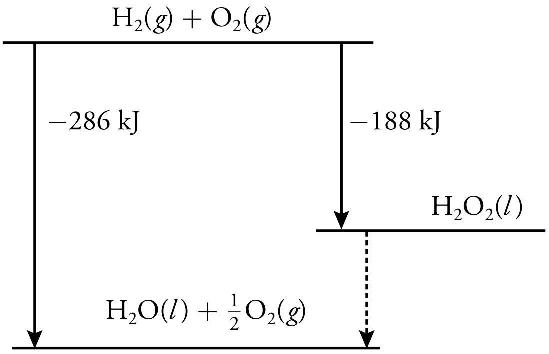
$$H_2(g) + O_2(g) \longrightarrow H_2O_2(l) \qquad \Delta H° = -188 \text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -286 \text{ kJ}$$

■ **Analysis:** In an enthalpy diagram, the reactions are written so as to show the amount of heat gained or lost by the reactants to form the products. In this question, we will be comparing one overall reaction.

■ **Assembling the Tools:** Three tools will be necessary to solve this problem. The first will be the tool for drawing enthalpy diagrams in which we will place the reactants and products and their states on the energy scale. The second will be the tool for deciding the algebraic sign of $\Delta H°$, that is, which way the arrows point: up for endothermic reactions or down for exothermic reactions. Finally, for the third tool, we will need to use the given thermochemical equations and the fact that enthalpies of reactions are state functions to calculate the enthalpy for the decomposition of $H_2O_2(l)$.

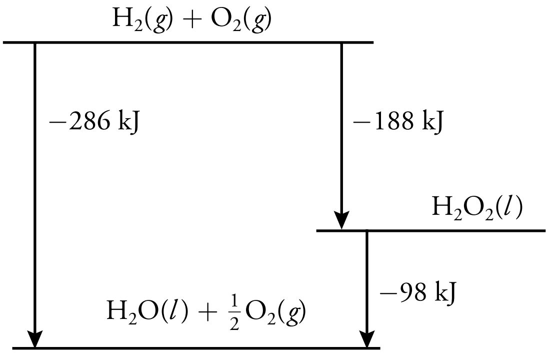
■ **Solution:** The two given reactions are exothermic, so their values of $\Delta H°$ will be associated with downward-pointing arrows. The highest enthalpy level, therefore, must be for the elements themselves, $H_2(g)$ and $O_2(g)$. Notice that the first reaction requires an entire mole of O_2, whereas the second needs only $\frac{1}{2}$ mol of O_2. On the top line we'll include enough O_2 for the formation of H_2O_2 by the first reaction. The lowest level must be for the product of the reaction with the largest negative $\Delta H°$, the formation of water by the second equation. Keep in mind that the second reaction only needs a half a mole of O_2, so this will leave $\frac{1}{2}O_2(g)$ unreacted when we form $H_2O(l)$, as indicated on the bottom line. The enthalpy level for the H_2O_2, formed by a reaction with the less negative $\Delta H°$, must be in between.



Notice that the gap on the right side (represented by the dashed arrow) corresponds exactly to the change of $H_2O_2(l)$ into $H_2O(l) + \frac{1}{2}O_2(g)$, the reaction for which we seek $\Delta H°$. This enthalpy separation corresponds to the difference between the enthalpy changes −286 kJ and −188 kJ. Thus for the decomposition of $H_2O_2(l)$ into $H_2O(l)$ and $\frac{1}{2}O_2(g)$,

$$\Delta H° = [-286 \text{ kJ} - (-188 \text{ kJ})] = -98 \text{ kJ}$$

Our completed enthalpy diagram is as follows, indicating that $\Delta H°$ for the decomposition of 1 mol of $H_2O_2(l)$ is −98 kJ.



■ **Is the Answer Reasonable?** First, be sure that the chemical formulas are arrayed properly on the horizontal lines in the enthalpy diagram. The arrows pointing downward should indicate negative values of $\Delta H°$. These arrows must be consistent *in direction* with the given equations (in other words, they must point from reactants to products). Finally, notice that the total amount of energy associated with the two-step process—namely, (−188 kJ) plus (−98 kJ)—equals −286 kJ, the energy for the one-step process.

Practice Exercises

7.11 | Two oxides of copper can be made from copper by the following reactions.

$$2Cu(s) + O_2(g) \longrightarrow 2CuO(s) \qquad \Delta H° = -310 \text{ kJ}$$

$$2Cu(s) + \tfrac{1}{2}O_2(g) \longrightarrow Cu_2O(s) \qquad \Delta H° = -169 \text{ kJ}$$

Using these data, construct an enthalpy diagram that can be used to find $\Delta H°$ for the reaction $Cu_2O(s) + \frac{1}{2}O_2(g) \longrightarrow 2CuO(s)$. Is the reaction endothermic or exothermic? (*Hint:* Remember, an arrow points down for a negative $\Delta H°$ and up for a positive $\Delta H°$.)

7.12 | Consider the following thermochemical equations:

$$\tfrac{1}{2}\mathrm{N_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO}(g) \qquad \Delta H^\circ = +90.4\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \qquad \Delta H^\circ = -56.6\ \mathrm{kJ}$$

Using these data, construct an enthalpy diagram that can be used to find ΔH° for the reaction $\tfrac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g)$. Is this reaction endothermic or exothermic?

Heats of Reaction from Hess's Law

Enthalpy diagrams, although instructive, are not necessary to calculate ΔH° for a reaction from known thermochemical equations. Using the tools for manipulating equations, we ought to be able to calculate ΔH° values simply by algebraic summing. G. H. Hess was the first to realize this, so the associated law is called **Hess's law of heat summation** or, simply, **Hess's law.**

■ Germain Henri Hess (1802–1850) anticipated the law of conservation of energy in the law named after him.

Hess's Law
The value of ΔH° for any reaction that can be written in steps equals the sum of the values of ΔH° of each of the individual steps.

TOOLS
Hess's law

For example, suppose we add the two equations in Practice Exercise 7.12 and then cancel anything that's the same on both sides.

$$\begin{array}{c}
\tfrac{1}{2}\mathrm{N_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO}(g)\\
\mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g)\\
\hline
\tfrac{1}{2}\mathrm{N_2}(g) + \cancel{\mathrm{NO}(g)} + \underbrace{\tfrac{1}{2}\mathrm{O_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g)}_{\mathrm{O_2}(g)} \longrightarrow \cancel{\mathrm{NO}(g)} + \mathrm{NO_2}(g)
\end{array}$$

Notice that we've combined the two $\tfrac{1}{2}\mathrm{O_2}(g)$ to give $\mathrm{O_2}(g)$. Rewriting the equation gives

$$\tfrac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g)$$

This is the equation for which we were asked to determine ΔH°. According to Hess's law, we should be able to obtain ΔH° for this reaction by simply adding the ΔH° values for the equations we've added.

$$\Delta H^\circ = (+90.4\ \mathrm{kJ}) + (-56.6\ \mathrm{kJ}) = +33.8\ \mathrm{kJ}$$

This was the answer to Practice Exercise 7.12. Thus, we've added the two given equations to obtain the desired equation, and we've added their ΔH° values to obtain the desired ΔH°.

The chief use of Hess's law is to calculate the enthalpy change for a reaction for which such data cannot be determined experimentally or are otherwise unavailable. Often this requires that we manipulate equations, so let's recapitulate the few rules that govern these operations.

Rules for Manipulating Thermochemical Equations

1. When an equation is reversed—written in the opposite direction—the sign of ΔH° must also be reversed.[4]
2. Formulas canceled from both sides of an equation must be for the substance in identical physical states.
3. If all the coefficients of an equation are multiplied or divided by the same factor, the value of ΔH° must likewise be multiplied or divided by that factor.

TOOLS
Manipulating thermochemical equations

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[4] To illustrate, the reverse of the equation,

$$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ = -394\ \mathrm{kJ}$$

is the following equation.

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{C}(s) + \mathrm{O_2}(g) \qquad \Delta H^\circ = +394\ \mathrm{kJ}$$

Example 7.9
Using Hess's Law

Carbon monoxide is often used in metallurgy to remove oxygen from metal oxides and thereby give the free metal. The thermochemical equation for the reaction of CO with iron(III) oxide, Fe_2O_3, is

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^\circ = -26.7 \text{ kJ}$$

Use this equation and the equation for the combustion of CO,

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -283.0 \text{ kJ}$$

to calculate the value of ΔH° for the following reaction:

$$2Fe(s) + \tfrac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$$

■ **Analysis:** We are given two thermochemical equations and are asked to find ΔH° for the third equation. We will need to manipulate the first two equations in order for them to give the third equation when they are added together.

■ **Assembling the Tools:** The tools will be Hess's law and the rules for manipulating thermochemical equations.

■ **Solution:** In this problem, we cannot simply add the two given equations, because this will not produce the equation we want. We first have to manipulate these equations so that when we add them we will get the target equation. In performing these adjustments, we have to keep our eye on our target—the final desired equation. When we've done this, we can then add the adjusted ΔH° values to obtain the desired ΔH°.

We can manipulate the two given equations as follows.

Step 1. We begin by trying to get the iron atoms to come out right. The target equation must have 2Fe on the *left*, but the first equation above has 2Fe to the *right* of the arrow. To move it to the left, we reverse the *entire* equation, remembering also to reverse the sign of ΔH°. This also puts Fe_2O_3 to the right of the arrow, which is where it needs to be. Now we have

$$2Fe(s) + 3CO_2(g) \longrightarrow Fe_2O_3(s) + 3CO(g) \qquad \Delta H^\circ = +26.7 \text{ kJ}$$

Step 2. There must be $\frac{3}{2}O_2$ on the left, and we must be able to cancel *three* CO and *three* CO_2 when the equations are added. If we multiply the second of the equations given above by 3, including the value for ΔH°, we will obtain the necessary coefficients. When we have done this, we have

$$3CO(g) + \tfrac{3}{2}O_2(g) \longrightarrow 3CO_2(g) \qquad \Delta H^\circ = 3 \times (-283.0 \text{ kJ}) = -849.0 \text{ kJ}$$

Now let's put our two equations together and find the answer:

$$\begin{array}{lll}
 & 2Fe(s) + 3CO_2(g) \longrightarrow Fe_2O_3(s) + \cancel{3CO(g)} & \Delta H^\circ = +26.7 \text{ kJ} \\
 & \cancel{3CO(g)} + \tfrac{3}{2}O_2(g) \longrightarrow 3CO_2(g) & \Delta H^\circ = -849.0 \text{ kJ} \\
\hline
\text{Sum:} & 2Fe(s) + \tfrac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) & \Delta H^\circ = -822.3 \text{ kJ}
\end{array}$$

Thus, the value of ΔH° for the oxidation of 2 mol Fe(*s*) to 1 mol $Fe_2O_3(s)$ is −822.3 kJ. (The reaction is *very* exothermic.)

■ **Is the Answer Reasonable?** There is no quick "head check," but for each step, double-check that you have heeded the rules for manipulating thermochemical equations. Also, be careful with the algebraic signs when adding the ΔH° values.

Practice Exercises

7.13 | Consider the thermochemical equation

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285.9 \text{ kJ}$$

What is the value of ΔH° for the following reaction?

$$3H_2O(l) \longrightarrow 3H_2(g) + \frac{3}{2}O_2(g)$$

(*Hint:* How does altering the coefficients and changing direction change ΔH°?)

7.14 | Given the following thermochemical equations,

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H^\circ = -113.2 \text{ kJ}$$
$$2N_2O(g) + 3O_2(g) \longrightarrow 4NO_2(g) \qquad \Delta H^\circ = -28.0 \text{ kJ}$$

calculate ΔH° for the reaction $N_2O(g) + \frac{1}{2}O_2(g) \longrightarrow 2NO(g)$

7.15 | Ethanol, C_2H_5OH, is made industrially by the reaction of water with ethylene, C_2H_4. Calculate the value of ΔH° for the reaction

$$C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$$

given the following thermochemical equations:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -1411.1 \text{ kJ}$$
$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H^\circ = -1367.1 \text{ kJ}$$

7.9 | Standard Heats of Reaction

Enormous databases of thermochemical equations have been compiled to make it possible to calculate almost any heat of reaction using Hess's law. The most frequently tabulated reactions are combustion reactions, phase changes, and formation reactions. We'll discuss the enthalpy changes that accompany phase changes in Chapter 12.

The **standard heat of combustion, ΔH°_c,** of a substance is the amount of heat released when one mole of a **fuel** substance is completely burned in pure oxygen gas, with all reactants and products brought to 25 °C and 1 bar of pressure. All carbon in the fuel becomes carbon dioxide gas, and all of the fuel's hydrogen becomes liquid water. *Combustion reactions are always exothermic*, so ΔH°_c is always negative.

Example 7.10
Writing an Equation for a Standard Heat of Combustion

How many moles of carbon dioxide gas are produced by a gas-fired power plant for every 1.00 MJ (megajoule) of energy it produces? The plant burns methane, $CH_4(g)$, for which ΔH°_c is −890 kJ/mol.

■ **Analysis:** We can restate the problem as an equivalency relation,

$$? \text{ mol } CO_2(g) \Leftrightarrow 1.00 \text{ MJ released}$$

We need to link moles of carbon dioxide with megajoules of heat produced.

■ **Assembling the Tools:** The tool we will use is the balanced thermochemical equation. For thermochemical equations of combustion reactions, when a hydrocarbon burns, the products are CO_2 and H_2O. The first step in the solution will be to write a balanced chemical equation for the reaction of CH_4 with O_2. Because ΔH°_c gives the heat evolved *per mole* of CH_4, we will have to be sure the coefficient of CH_4 is 1. In the equation CH_4, O_2, and CO_2 will be gases and H_2O will be a liquid (because that's the standard form of H_2O at 25 °C.)

Once we have the thermochemical equation, the coefficients will let us relate moles of CO_2 to kilojoules of heat released. To relate megajoules with kilojoules, our tools will be the SI prefixes *kilo* and *mega*.

$$1\text{ MJ} = 10^6\text{ J}$$
$$1\text{ kJ} = 10^3\text{ J}$$

Solution: First, we write and balance the thermochemical equation, remembering that $\Delta H°$ is $\Delta H°_c$.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H°_c = -890\text{ kJ}$$

Thus, 1 mol CO_2 is formed for every 890 kJ of heat that is released. The number of moles of CO_2 released for the production of 1.00 MJ of energy is

$$1.00\,\cancel{\text{MJ}} \times \frac{10^6\,\cancel{\text{J}}}{1\,\cancel{\text{MJ}}} \times \frac{1\,\cancel{\text{kJ}}}{10^3\,\cancel{\text{J}}} \times \frac{1\text{ mol CO}_2}{890\,\cancel{\text{kJ}}} = 1.12\text{ mol CO}_2$$

Is the Answer Reasonable? When 1 mol CH_4 burns, 890 kJ are released. This is just a little less than 1000 kJ (or 1 MJ), so the amount of CH_4 needed to release 1 MJ should be a bit larger than 1 mol. Our answer, 1.12 mol CO_2, is reasonable.

Practice Exercises

7.16 | The heat of combustion, $\Delta H°_c$, of acetone, C_3H_6O, is 1790.4 kJ/mol. How many kilojoules of heat are evolved in the combustion of 12.5 g of acetone? (*Hint:* Calculate the molar mass of acetone.)

7.17 | *n*-Octane, $C_8H_{18}(l)$, has a standard heat of combustion of 5450.5 kJ/mol. A 15 gallon automobile fuel tank could hold about 480 moles of *n*-octane. How much heat could be produced by burning a full tank of *n*-octane?

Standard Heats of Formation and Hess's Law Equation

The **standard enthalpy of formation, $\Delta H°_f$,** of a substance, also called its **standard heat of formation,** is the amount of heat absorbed or evolved when specifically *one mole* of the substance is formed at 25 °C and 1 bar from its elements in their *standard states.* An element is in its **standard state** when it is at 25 °C and 1 bar and in its most stable form and physical state (solid, liquid, or gas). Oxygen, for example, is in its standard state only as a gas at 25 °C and 1 bar and only as O_2 molecules, not as O atoms or O_3 (ozone) molecules. Carbon must be in the form of graphite, not diamond, to be in its standard state, because the graphite form of carbon is the more stable form under standard conditions.

Older thermochemical data used a standard pressure of 1 atm, not 1 bar. Because 1 atm = 1.01325 bar, the new definition made little difference in tabulated heats of reaction.

Standard enthalpies of formation for a variety of substances are given in Table 7.2, and a more extensive table of standard heats of formation can be found in Appendix C. Notice in particular that **all values of $\Delta H°_f$ for the elements in their standard states are zero.** (Forming an element *from itself* would yield no change in enthalpy.) In most tables, values of $H°_f$ for the elements are not included for this reason.

It is important to remember the meaning of the subscript f in the symbol $\Delta H°_f$. It is applied to a value of $\Delta H°$ only when *one mole* of the substance is formed *from its elements in their standard states*. Consider, for example, the following four thermochemical equations and their corresponding values of $\Delta H°$.

Table 7.2 Standard Enthalpies of Formation of Typical Substances

Substance	ΔH_f° (kJ mol^{-1})	Substance	ΔH_f° (kJ mol^{-1})
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgBr(s)$	−100.4	$HBr(g)$	−36
$AgCl(s)$	−127.0	$HCl(g)$	−92.30
$Al(s)$	0	$HI(g)$	26.6
$Al_2O_3(s)$	−1669.8	$HNO_3(l)$	−173.2
$C(s)$ (graphite)	0	$H_2SO_4(l)$	−811.32
$CO(g)$	−110.5	$HC_2H_3O_2(l)$	−487.0
$CO_2(g)$	−393.5	$Hg(l)$	0
$CH_4(g)$	−74.848	$Hg(g)$	60.84
$CH_3Cl(g)$	−82.0	$I_2(s)$	0
$CH_3I(g)$	14.2	$K(s)$	0
$CH_3OH(l)$	−238.6	$KCl(s)$	−435.89
$CO(NH_2)_2(s)$ (urea)	−333.19	$K_2SO_4(s)$	−1433.7
$CO(NH_2)_2(aq)$	−391.2	$N_2(g)$	0
$C_2H_2(g)$	226.75	$NH_3(g)$	−46.19
$C_2H_4(g)$	52.284	$NH_4Cl(s)$	−315.4
$C_2H_6(g)$	−84.667	$NO(g)$	90.37
$C_2H_5OH(l)$	−277.63	$NO_2(g)$	33.8
$Ca(s)$	0	$N_2O(g)$	81.57
$CaBr_2(s)$	−682.8	$N_2O_4(g)$	9.67
$CaCO_3(s)$	−1207	$N_2O_5(g)$	11
$CaCl_2(s)$	−795.0	$Na(s)$	0
$CaO(s)$	−635.5	$NaHCO_3(s)$	−947.7
$Ca(OH)_2(s)$	−986.59	$Na_2CO_3(s)$	−1131
$CaSO_4(s)$	−1432.7	$NaCl(s)$	−411.0
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	−1575.2	$NaOH(s)$	−426.8
$CaSO_4 \cdot 2H_2O(s)$	−2021.1	$Na_2SO_4(s)$	−1384.5
$Cl_2(g)$	0	$O_2(g)$	0
$Fe(s)$	0	$Pb(s)$	0
$Fe_2O_3(s)$	−822.2	$PbO(s)$	−219.2
$H_2(g)$	0	$S(s)$	0
$H_2O(g)$	−241.8	$SO_2(g)$	−296.9
$H_2O(l)$	−285.9	$SO_3(g)$	−395.2

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f^\circ = -285.9 \text{ kJ/mol}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H^\circ = -571.8 \text{ kJ}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -283.0 \text{ kJ}$$

$$2H(g) + O(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -971.1 \text{ kJ}$$

Only in the first equation is ΔH° given the subscript f. It is the only reaction that satisfies both of the conditions specified previously for standard enthalpies of formation. The second equation shows the formation of *two* moles of water, not one. The third involves a *compound* as one of the reactants. The fourth involves the elements as *atoms*, which are *not standard states* for these elements. Also notice that the units of ΔH_f° are kilojoules *per mole,* not just kilojoules, because the value is for the formation of 1 mol of the compound (from its elements). We can obtain the enthalpy of formation of two moles of water (ΔH° for the second equation) simply by multiplying the ΔH_f° value for 1 mol of H_2O by the factor 2 mol $H_2O(l)$.

$$\left(\frac{-285.9 \text{ kJ}}{1 \text{ mol } H_2O(l)}\right) \times 2 \text{ mol } H_2O(l) = -571.8 \text{ kJ}$$

Example 7.11
Writing an Equation for a Standard Heat of Formation

What equation must be used to represent the formation of nitric acid, $HNO_3(l)$, when we want to include its value of ΔH_f°?

Analysis: Answering the question requires that we know the definition of ΔH_f°, which demands that the equation must show only *one mole* of the product. We must also be careful to include the physical states.

Assembling the Tools: The first tool we will use is the one for writing thermochemical equations and writing equations for the standard heat of formation of a compound. We begin with its formula and take whatever fractions of moles of the elements are required to make it. The other tool we will use is Table 7.2, which gives the value of ΔH_f° for $HNO_3(l)$, -173.2 kJ mol^{-1}.

Solution: The three elements, H, N, and O, all occur as diatomic molecules in the gaseous state, so the following fractions of moles supply exactly enough of each to make one mole of HNO_3.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}N_2(g) + \tfrac{3}{2}O_2(g) \longrightarrow HNO_3(l) \qquad \Delta H_f^\circ = -173.2 \text{ kJ mol}^{-1}$$

Is the Answer Reasonable? The answer correctly shows only 1 mol of HNO_3, and this governs the coefficients for the reactants. So, simply check to make sure everything is balanced.

Practice Exercises

7.18 | Write the thermochemical equation that would be used to represent the standard heat of formation of $NH_4Cl(s)$. (*Hint:* Be sure you show substances in their standard states.)

7.19 | Write the thermochemical equation that would be used to represent the standard heat of formation of sodium bicarbonate, $NaHCO_3(s)$.

Standard enthalpies of formation are useful because they provide a convenient method for applying Hess's law without having to manipulate thermochemical equations. To see how this works, let's look again at Example 7.8, where we calculated ΔH_f° for the decomposition of H_2O_2.

$$H_2O_2(l) \longrightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

The two equations we used were

$$(1)\quad H_2(g)+O_2(g)\longrightarrow H_2O_2(l)\qquad \Delta H_f^\circ\,(1)=-188\text{ kJ}$$

$$(2)\quad H_2(g)+\tfrac{1}{2}O_2(g)\longrightarrow H_2O(l)\qquad \Delta H_f^\circ\,(2)=-286\text{ kJ}$$

This time we have numbered the equations and identified the enthalpy changes as ΔH_f° because in each case we're forming one mole of the compound from elements in their standard states. To combine these equations to find ΔH° for the decomposition of H_2O_2, we have to reverse equation (1), which means we change the sign of its ΔH.

$$\begin{array}{lll}
\text{(1 reversed)} & H_2O_2(l)\longrightarrow H_2(g)+O_2(g) & \Delta H^\circ=-\Delta H_f^\circ\,(1)=+188\text{ kJ}\\
(2) & H_2(g)+\tfrac{1}{2}O_2(g)\longrightarrow H_2O(l) & \Delta H_f^\circ\,(2)=-286\text{ kJ}\\
\hline
\text{Sum} & H_2O_2(l)\longrightarrow H_2O(l)+\tfrac{1}{2}O_2(g) & \Delta H^\circ=[\Delta H_f^\circ\,(2)]+[-\Delta H_f^\circ\,(1)]\\
 & & =-286\text{ kJ}+(+188\text{ kJ})\\
 & & =-98\text{ kJ}
\end{array}$$

■ We can also use heats of combustion in Hess's law calculations. In doing so, remember that the heats of combustion of elements are zero and that simple products such as CO_2 and H_2O are obtained from the combustion of the elements C and H_2. Use heats of combustion for all reactants and all products, *or* use heats of formation for all reactants and all products, but don't mix them.

Thus, the desired ΔH° was obtained by subtracting the ΔH_f° for the reactant (H_2O_2) from the ΔH_f° for the product (H_2O). In fact, this works for *any* reaction where we know the heats of formation of all of the reactants and products. So, if we're working with heats of formation, Hess's law can be restated as follows: the net $\Delta H^\circ_{\text{reaction}}$ equals the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants, each ΔH_f° value multiplied by the appropriate coefficient given by the thermochemical equation. In other words, we can express Hess's law in the form of the **Hess's law equation:**

$$\Delta H^\circ_{\text{reaction}}=\begin{bmatrix}\text{sum of }\Delta H_f^\circ\text{ of all}\\ \text{of the products}\end{bmatrix}-\begin{bmatrix}\text{sum of }\Delta H_f^\circ\text{ of all}\\ \text{of the reactants}\end{bmatrix}\qquad(7.14)$$

TOOLS

Hess's law equation

As long as we have access to a table of standard heats of formation, using Equation 7.14 avoids having to manipulate a series of thermochemical equations. Finding the $\Delta H^\circ_{\text{reaction}}$ reduces to performing arithmetic, as we see in the next example.

Example 7.12

Using Hess's Law and Standard Enthalpies of Formation

Some chefs keep baking soda, $NaHCO_3$, handy to put out grease fires. When thrown on the fire, baking soda partly smothers the fire and the heat decomposes it to give CO_2, which further smothers the flame. The equation for the decomposition of $NaHCO_3$ is

$$2NaHCO_3(s)\longrightarrow Na_2CO_3(s)+H_2O(l)+CO_2(g)$$

Use the data in Table 7.2 to calculate ΔH° for this reaction in kilojoules.

■ **Analysis:** We are being asked to calculate ΔH° for a reaction. We are not given a series of reactions to manipulate, but we are asked to use the information in Table 7.2, the ΔH_f° for the reactants and the products. Therefore, we will use Hess's law equation to calculate $\Delta H^\circ_{\text{reaction}}$.

■ **Assembling the Tools:** Hess's law equation (Equation 7.14) is our basic tool for computing values of ΔH°. We will subtract the sum of the ΔH° for the reactants from the sum of the ΔH° for the products to calculate $\Delta H^\circ_{\text{reaction}}$. For each of the reactants and products, we compute its ΔH° by multiplying its ΔH_f° (from Table 7.2) by its coefficient in the balanced chemical equation.

Solution: First, let's set up the calculation using symbols for the quantities we will use.

$$\Delta H^\circ = [1 \text{ mol } Na_2CO_3(s) \times \Delta H^\circ_{f\,Na_2CO_3(s)} + 1 \text{ mol } H_2O(l) \times \Delta H^\circ_{f\,H_2O(l)} + 1 \text{ mol } CO_2(g) \times \Delta H^\circ_{f\,CO_2(g)}] - [2 \text{ mol } NaHCO_3(s) \times \Delta H^\circ_{f\,NaHCO_3(s)}]$$

Now we go to Table 7.2 to find the values of ΔH°_f for each substance in its proper physical state.

$$\Delta H^\circ = \left[(1 \ \cancel{\text{mol } Na_2CO_3}) \times \left(\frac{-1131 \text{ kJ}}{\cancel{\text{mol } Na_2CO_3}}\right) + 1 \ \cancel{\text{mol } H_2O} \times \left(\frac{-285.9 \text{ kJ}}{\cancel{\text{mol } H_2O}}\right) + 1 \ \cancel{\text{mol } CO_2} \times \left(\frac{-393.5 \text{ kJ}}{\cancel{\text{mol } CO_2}}\right)\right] - \left[2 \ \cancel{\text{mol } NaHCO_3} \times \left(\frac{-947.7 \text{ kJ}}{\cancel{\text{mol } NaHCO_3}}\right)\right]$$

This reduces to

$$\begin{aligned}\Delta H^\circ &= (-1810 \text{ kJ}) - (-1895 \text{ kJ}) \\ &= +85 \text{ kJ}\end{aligned}$$

Thus, under standard conditions, the reaction is endothermic by 85 kJ. (Notice that we did not have to manipulate any equations.)

Is the Answer Reasonable? Double-check that all of the coefficients found in the chemical equation are correctly applied as multipliers on the ΔH°_f quantities. Be sure that the *signs* of the values of ΔH°_f have all been carefully used. Keeping track of the algebraic signs requires particular care and is the greatest source of error in these calculations. Also check to be sure you've followed the correct order of subtraction specified in Equation 7.14. In other words, have you subtracted the ΔH° of the *reactants* from the ΔH° of the *products*?

Practice Exercises

7.20 | Use heats of formation data from Table 7.2 to calculate ΔH° for the reaction $CaCl_2(s) + H_2SO_4(l) \longrightarrow CaSO_4(s) + 2HCl(g)$. (*Hint:* Be sure to follow the correct order of subtraction.)

7.21 | Write thermochemical equations corresponding to ΔH°_f for $SO_3(g)$ and $SO_2(g)$ and show how they can be manipulated to calculate ΔH° for the following reaction:

$$SO_3(g) \longrightarrow SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\circ = ?$$

Use Equation 7.14 to calculate ΔH° for the reaction using the heats of formation of $SO_3(g)$ and $SO_2(g)$. How do the answers compare?

7.22 | Calculate ΔH° for the following reactions:

(a) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(b) $NaOH(s) + HCl(g) \longrightarrow NaCl(s) + H_2O(l)$

CHEMISTRY AND CURRENT AFFAIRS 7.2

Runaway Reactions: The Importance of Thermodynamics

In 1998, a runaway reaction occurred in a reaction vessel in which a dye was being made at a Morton International Plant in Paterson, N.J. The reaction overheated, causing pressure to build up inside the vessel. The vessel ruptured, ejecting the contents through the roof. The resultant vapor cloud ignited and produced an explosion and fire that injured nine employees and destroyed the facility (Figure 1).

Most chemical reactions are exothermic. The heat given off by the reaction will raise the temperature of the reaction mixture unless it is removed. The heat may be removed through normal losses to the surroundings, by deliberate cooling, such as pumping a cold fluid around the outside (jacket) of the reaction vessel, or by other techniques. When the rate at which the reaction generates heat is faster than the rate at which the equipment can remove the heat, a point of no return is reached (Figure 2). The reaction mixture will heat up out of control. As the temperature rises, the reaction rate increases exponentially, thus increasing the rate at which heat is released and causing the temperature to rise even faster. As the temperature rises, the solvent and any other volatile components turn into gases, which increases the pressure inside

Figure 1 *(Bill Tompkins)*

the reactor. In a properly designed reactor, a safety vent will open to relieve the pressure. However, if this vent is not large enough, the pressure will eventually cause the vessel to rupture, releasing a mixture of liquid and vapor. If the vapor cloud is flammable and it finds an ignition source, an explosion and fireball can result.

Runaway reactions can occur in the laboratory as well as in manufacturing. To prevent runaway reactions and their potentially disastrous results, it is important to know how much heat a reaction will release, how fast the heat is released, and how fast the heat can be removed from the reaction equipment. Hazards can be anticipated by calculating the potential adiabatic temperature rise, pressure increases, and vapor volumes generated.

In the Morton International incident, *ortho*-nitrochlorobenzene (*o*-NCB) was reacted with 2-ethylhexylamine (2-EHA) to form Automate yellow 96 Dye.

The heat of reaction was known from calorimetry experiments, but not included in the incident report. However, the heat of reaction can be estimated using standard heats of formation for the exact compounds, or for simpler compounds as long as the same types of bonds are being broken and formed. Using compounds called chlorobenzene and methylamine as model compounds for the reaction, a heat of reaction of −176 kJ/mol *o*-NCB is estimated. At 195 °C, the Yellow 96 starts to decompose exothermically and generates gaseous by-products.

To avoid having to handle the *o*-NCB several times, since it is a poison, all of the reactants were added at once, and the mixture was slowly heated up in stages. At low temperatures, the reaction was slow and the heat could be removed by passing cold water through the reactor jacket. As the reaction progressed, it slowed down and the reactor was heated. This process continued until the reaction was completed at 150 °C. This staged heating procedure is inherently more hazardous: if the reaction is heated too quickly, it could get out of control.

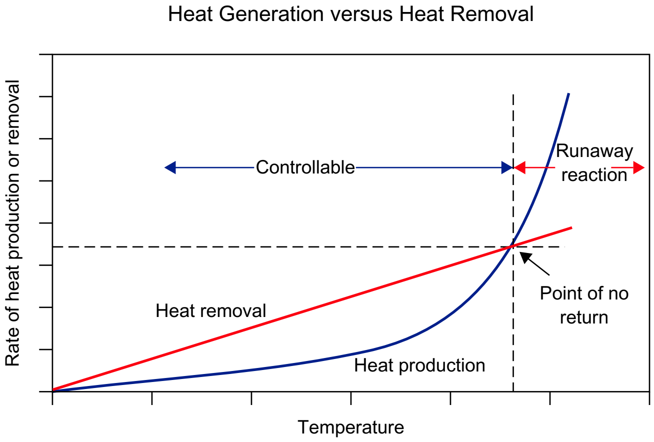

Figure 2 If the reaction temperature exceeds the point of no return, heat generation will exceed the ability of the surroundings to remove the heat and the reaction will run away uncontrolled.

The size of the process was increased from a 1000 gallon spherical reactor to a 2000 gallon spherical reactor. When switching to larger reactors, the surface area available for heat removal increases approximately with the square of the diameter. The volume, which corresponds to reaction mass and total heat generated, increases approximately with the cube of the diameter. Thus, doubling the reactor volume corresponds to only about 1.6 times the surface area available for heat removal. At this larger scale, 50% of the batches had small runaway reactions as compared to 20% for the smaller scale reactions.

On the day of the accident, the operators heated the reaction vessel to 90 °C. They heated the reactor too quickly, so very little of the reaction had occurred at the lower temperatures at which the heat could be safely removed. Now, most of the reactants remained and were reacting rapidly. The temperature overshot the point of no return and continued to rise rapidly despite the application of cooling water. The temperature rose past the 150 °C maximum operating temperature. At about 185 °C, the pressure had increased enough to cause the relief vent to open. The temperature continued to rise and went from 190 °C to 260 °C in less than 30 seconds. With the onset of gaseous decomposition of the product, the vent was not large enough to accommodate the excess gases and pressure, and the reactor ruptured.

Contributed by Gary Buskes

Source: U. S. Chemical Safety and Hazard Investigation Board
Office of External Relations
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Washington, DC 20037
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Analyzing and Solving Multi-Concept Problems

In an experiment, 95.0 mL of 0.225 *M* silver nitrate was mixed rapidly with 47.5 mL of 0.225 *M* calcium chloride in a coffee cup calorimeter. If a reaction occurred, was it exothermic or endothermic? If the reaction started at 23.7 °C, what is the final temperature of the solution?

■ **Analysis** First, we may or may not have a reaction occurring. Since we are dealing with ionic compounds, we have to see whether a metathesis reaction occurs, something we studied in Chapter 5. If a reaction occurs, we will need to write out a balanced equation.

We will then need to determine whether the reaction is exothermic or endothermic. In order to do this, we will need to change the balanced equation into a thermochemical equation for the reaction.

Next, since this reaction is not performed on a 1 molar scale, we will need to calculate how many moles of reactants are present and how much energy is involved in this reaction.

Finally, in the last step, we will calculate the change in temperature of the solution.

■ **Strategy** The problem is now broken into four parts: (1) Writing and balancing the chemical equation and determining whether a reaction occurred; (2) calculating the heat of the reaction; (3) determining the amount of heat for the given amount of reactants using the molarity, volume, and the heat of reaction; and (4) determining how much the temperature of the solution changed.

PART 1

■ **Assembling the Tools** The first step is to write a balanced equation for a metathesis reaction and then use the solubility rules to determine whether a reaction occurs.

■ **Solution** The products of a metathesis reaction are AgCl and $Ca(NO_3)_2$, and from the solubility rules we know that AgCl is insoluble in water. The molecular equation for the reaction is

$$2AgNO_3(aq) + CaCl_2(aq) \longrightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$

Let's also set up the ionic and net ionic equations.

$$2Ag^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow 2AgCl(s) + Ca^{2+}(aq) + 2NO_3^-(aq)$$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

These are the equations we will use in Part 2.

PART 2

■ **Assembling the Tools** Now that we have the balanced chemical equation, we need to write the thermochemical equation for the reaction. We will use Hess's law equation, Equation 7.14, which uses the heats of formation and the coefficients of the balanced chemical equation to determine the heat of the reaction. Since the reactants are in solution, we will use the $\Delta H°$ values for the ions. We can use the net ionic equation to calculate the heat of the reaction because the spectator ions do not change their heats of formation in going from reactants to products.

■ **Solution** We will proceed with the calculation by setting up the equation we will need:

$$\Delta H° = [1 \text{ mol AgCl}(s) \times \Delta H°_{f\,AgCl(s)}] - [1 \text{ mol Ag}^+(aq) \times \Delta H°_{f\,Ag^+(aq)} + 1 \text{ mol Cl}^-(aq) \times \Delta H°_{f\,Cl^-(aq)}]$$

Unfortunately, Table 7.2 does not have all of the information that we need, but in Appendix C is a more comprehensive list of heats of formation, so we will use Table C.1 of Appendix C to find the data that we need and then substitute the values into the equation.

$$\Delta H° = \left[(1 \cancel{\text{mol AgCl}} \times \left(\frac{-127.0 \text{ kJ}}{\cancel{\text{mol AgCl}}} \right) \right] - \left[1 \cancel{\text{mol Ag}^+} \times \left(\frac{+105.58 \text{ kJ}}{\cancel{\text{mol Ag}^+}} \right) + 1 \cancel{\text{mol Cl}^-} \times \left(\frac{-167.2 \text{ kJ}}{\cancel{\text{mol Cl}^-}} \right) \right]$$

This becomes

$$\begin{aligned}\Delta H^\circ &= (-127.0\text{ kJ}) - (-61.62\text{ kJ})\\ &= -65.4\text{ kJ}\end{aligned}$$

This reaction gives off 65.4 kJ of heat for 1 mol of $AgNO_3$ and the thermochemical equation is written as

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) \qquad \Delta H^\circ = -65.4\text{ kJ}$$

PART 3

Assembling the Tools Now that we have the thermochemical equation for the reaction, we need to calculate the moles of silver and chloride in the solution and use that information to determine how much heat was lost by the reaction. From the equation for molarity:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in L}}$$

we can rearrange it to find the moles of the ions:

$$\text{number of moles of solute} = (\text{molarity}) \times (\text{volume of solution in L})$$

Using the moles of the reactants, we can calculate how much heat is given off:

$$q_{\text{reaction}} = \text{actual moles of reactant} \times \frac{\text{heat of reaction}}{\text{mol of reactant}}$$

Solution We need to calculate the number of moles of silver and the number of moles of chloride used in the reaction:

$$\begin{aligned}\text{mol } Ag^+ &= 0.0950\ \cancel{\text{L } AgNO_3} \times \frac{0.225\ \cancel{\text{mol } AgNO_3}}{1\ \cancel{\text{L } AgNO_3}} \times \frac{1\text{ mol } Ag^+}{1\ \cancel{\text{mol } AgNO_3}}\\ &= 2.14 \times 10^{-2}\text{ mol } Ag^+\end{aligned}$$

$$\begin{aligned}\text{mol } Cl^- &= 0.0475\ \cancel{\text{L } CaCl_2} \times \frac{0.225\ \cancel{\text{mol } CaCl_2}}{1\ \cancel{\text{L } CaCl_2}} \times \frac{2\text{ mol } Cl^-}{1\ \cancel{\text{mol } CaCl_2}}\\ &= 2.14 \times 10^{-2}\text{ mol } Cl^-\end{aligned}$$

From the calculation, we can see that we have an equal molar amount of silver ions and chloride ions, so that we will make 2.14×10^{-2} mol AgCl. Now we can determine how much heat will be generated from this reaction by using the moles of AgCl formed and the amount of heat given off when one mole of AgCl is formed:

$$q_{\text{reaction}} = 2.14 \times 10^{-2}\ \cancel{\text{mol AgCl}} \times \frac{-65.4\text{ kJ}}{1\ \cancel{\text{mol AgCl}}} = -1.40\text{ kJ}$$

PART 4

Assembling the Tools For the last step, we will use the heat given off by the reaction to calculate the temperature of the solution using Equation 7.7,

$$q = ms\,\Delta t$$

where Δt is the temperature change for the system, s is the specific heat of water, and m is the mass of the water. We will also need to use Equation 7.8, which relates the heat given off by the reaction to the heat absorbed by the water:

$$q_{\text{reaction}} = -q_{\text{water}}$$

Solution The reaction gave off 1.40 kJ of heat. Since the reaction was carried out in a coffee cup calorimeter, we can assume that all of the heat was absorbed by the water, and so we get

$$q_{\text{reaction}} = -q_{\text{water}}$$

$$-1.40 \text{ kJ} = -(-1.40 \text{ kJ}) = 1.40 \text{ kJ} = 1.40 \times 10^3 \text{ J}$$

We will rearrange Equation 7.7 to solve for the change in temperature:

$$q = ms\,\Delta t$$

$$\Delta t = \frac{q}{ms}$$

Using this as the value for q using 4.184 J/g °C for the specific heat of water, and assuming that the density of water is 1 g/mL, so that the mass of the water is 95.0 + 47.5 g = 142.5 g,

$$\begin{aligned}\Delta t &= \frac{1.40 \times 10^3 \text{ J}}{142.5 \text{ g} \times 4.184 \text{ J/g °C}}\\ &= 2.35 \text{ °C}\end{aligned}$$

The temperature went up by 2.35 °C, so the final temperature is 26.1 °C. To make sure that we answered all of the questions, we will now go back and answer them completely. A reaction occurred, and it was exothermic with the final temperature being 26.1 °C.

Are the Answers Reasonable? We can go through the reasoning again and check to make sure that we did not skip any steps. We can also look at the fact that the reaction is exothermic, and the water that absorbed the heat became slightly warmer. We can check our math, so it is always a good idea to write out our equations and the math.

Summary

Introduction. **Thermochemistry**, which deals with the energy absorbed or released in chemical reactions, is a part of **thermodynamics**, the study of energy transfer and energy transformation. **Heat** is energy (**thermal energy**) that transfers between objects having different temperatures. Heat continues to flow until the two objects come to the same temperature and **thermal equilibrium** is established.

Energy Is the Ability to Do Work or Supply Heat. An object has **kinetic** energy (KE) if it is moving $\text{KE} = \frac{1}{2}mv^2$ and **potential energy (PE)** when it experiences attractions or repulsions toward other objects. When objects that attract are moved apart, PE increases. Similarly, when objects that repel are pushed together, PE increases. Because electrical attractions and repulsions occur within atoms, molecules, and ions, substances have **chemical energy**, a form of **potential energy**. The particles that make up matter are in constant random motion, so they also possess kinetic energy, specifically, **molecular kinetic energy**. According to the **kinetic molecular theory**, the average molecular kinetic energy is directly proportional to the Kelvin temperature. According to the **law of conservation of energy**, energy can be neither created nor destroyed; instead, it can only be changed from one form to another. The SI unit of energy is the **joule**; 4.184 J = 1 cal (**calorie**). Larger units are the **kilojoule** (**kJ**) and **kilocalorie** (**kcal**), which is the same as the nutritional Calorie.

Internal Energy and Temperature. The **state** of a system is the list of properties that describe its current condition. The **internal energy** of a system, E, is a **state function,** which is a property that depends only on the current state of the system. E equals the sum of the system's molecular kinetic and potential energies. A change in E is defined as $\Delta E = E_{\text{final}} - E_{\text{initial}}$, although absolute amounts of E cannot be measured or calculated. For a chemical reaction, the definition translates to $\Delta E = E_{\text{products}} - E_{\text{reactants}}$. A positive value for ΔE, which can be measured, means a system absorbs energy from its surroundings during a change.

Measuring Heat. The boundary across which heat is transferred encloses the system (the object we're interested in). Everything else in the universe is the system's **surroundings**. The heat flow q is related to the temperature change Δt by $q = C\,\Delta t$, where C is the **heat capacity** of the system (the heat needed to change the temperature of the system by one degree Celsius). The heat capacity for a pure substance can be computed from its mass, m, using the equation $C = ms$, where s is the **specific heat** of the material (the heat needed to change the temperature of 1 g of a substance by 1 °C). Water has an unusually high specific heat. We can compute a heat flow when we know the mass and specific heat of an object using the equation $q = ms\,\Delta t$. The heat, q, is given a positive sign when it flows into a system and a negative sign when it flows out.

Energy Changes When Bonds Are Formed or Broken. Bond breaking increases potential energy (chemical energy); bond formation decreases potential energy (chemical energy). In an **exothermic** reaction, chemical energy is changed to molecular kinetic energy. If the system is **adiabatic** (no heat leaves it), the internal temperature increases. Otherwise, the heat has a tendency to leave the system. In **endothermic** reactions, molecular kinetic energy of the reactants is converted into potential energy of the products. This tends to lower the system's temperature and lead to a flow of heat into the system.

Heats of Reaction. The change in chemical potential energy in a reaction is the **heat of reaction, q**, which can be measured at constant volume or constant pressure. Pressure is the ratio of force to the area over which the force is applied. **Atmospheric pressure** is the pressure exerted by the mixture of gases in our atmosphere. When the volume change, ΔV, occurs at constant opposing pressure, P, the associated **pressure–volume work** (**expansion work**) is given by $w = -P\Delta V$. The energy expended in doing this pressure–volume work causes heats of reaction measured at constant volume (q_v) to differ numerically from heats measured at constant pressure (q_p).

The **first law of thermodynamics** says that no matter how the change in energy accompanying a reaction may be allocated between q and w, their sum, ΔE, is the same: $\Delta E = q + w$. The algebraic sign for q and w is negative when the system gives off heat to or does work on the surroundings. The sign is positive when the system absorbs heat or receives work energy done to it. When the volume of a system cannot change, as in a **bomb calorimeter**, w is zero, and **q_v** is the **heat of reaction at constant volume**, ΔE.

When the system is under conditions of constant pressure, the energy of the system is called its **enthalpy, H**. At constant pressure, $\Delta H = \Delta E + P\Delta V$. The **heat of reaction at constant pressure, q_p**, is the **enthalpy change,** ΔH. Its value differs from that of ΔE by the work involved in interacting with the atmosphere when the change occurs at constant atmospheric pressure. In general, the difference between ΔE and ΔH is quite small. Exothermic reactions have negative values of ΔH; endothermic changes have positive values.

Thermochemical Equations. A balanced chemical equation that includes both the enthalpy change and the physical states of the substances is called a **thermochemical equation**. Coefficients in a thermochemical equation represent mole quantities of reactants and products, so it is reasonable to have fractional coefficients such as $\frac{1}{2}$. Such equations can be added, reversed (reversing also the sign of ΔH), or multiplied by a constant multiplier (doing the same to ΔH). If formulas are canceled or added, they must be of substances in identical physical states.

The reference conditions for thermochemistry, called **standard conditions**, are 25 °C and 1 bar of pressure. An enthalpy change measured under these conditions is called the **standard enthalpy of reaction** or the **standard heat of reaction,** given the symbol **$\Delta H°$.**

Hess's law of heat summation is possible because enthalpy is a state function. Values of $\Delta H°$ can be determined *by the manipulation of any combination of thermochemical equations that add up to the final net equation. The units for $\Delta H°$ are generally joules or kilojoules.* An **enthalpy diagram** provides a graphical description of the enthalpy changes for alternative paths from reactants to products.

When the enthalpy change is for the complete combustion of one mole of a pure substance under standard conditions in pure oxygen, $\Delta H°$ is called the **standard heat of combustion** of the compound and is symbolized as $\Delta H_c°$.

When the enthalpy change is for the formation of *one* mole of a substance under standard conditions from its *elements in their standard states*, $\Delta H°$ is called the **standard heat of formation** of the compound and is symbolized as $\Delta H_f°$, (usually in units of kilojoules per mole, kJ mol^{-1}). The value of $\Delta H°$ for a reaction can be calculated from tabulated values of $\Delta H_f°$ using the **Hess's law equation**.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Kinetic energy (page 254)

Kinetic energy (KE) can be calculated from an object's mass, m, and its speed or velocity, v, using Equation 7.1: $\text{KE} = \frac{1}{2}mv^2$.

Potential energy changes (page 255)

You should know how potential energy varies when the distance changes between objects that attract or repel.

Heat capacity (page 260)

Heat capacity, C, makes it possible to determine heat by measuring a temperature change. Its units are energy divided by temperature (e.g., J °C^{-1}).

$$q = C\,\Delta t$$

The value of C depends on sample size and is an extensive property.

Specific heat capacity (page 261)

Also called specific heat, s, it is an intensive property. When mass, m, and temperature change, Δt, are known, q is calculated by the equation

$$q = ms\,\Delta t$$

Heat transfer (page 262)

When heat is transferred between two objects, the *size* of q is identical for both objects, but the algebraic signs of q are opposite.

$$q_1 = -q_2$$

First law of thermodynamics (page 269)

This law relates energy transfer in the forms of heat, q, and work, w, to the internal energy change, ΔE.

$$\Delta E = q + w$$

The algebraic sign of ΔH (page 273)

The sign of ΔH indicates the direction of energy flow.

For an endothermic change, ΔH is positive.
For an exothermic change, ΔH is negative.

Thermochemical equations (page 276)

They show enthalpy changes for reactions where the amounts of reactants and products in moles are represented by the coefficients. They can be manipulated and combined to determine heats of reactions for other reactions.

Enthalpy diagram (page 278)

We use enthalpy diagrams to provide a graphical picture of the enthalpy changes associated with a set of thermochemical equations that are combined to give some net reaction.

Hess's law (page 281)

Hess's law allows us to combine thermochemical equations to give a final desired equation and its associated $\Delta H°$. We adjust the coefficients and directions of the given equations and make appropriate adjustments to their $\Delta H°$ values, so the equations add to give the desired equation. Adding the adjusted $\Delta H°$ values gives the $\Delta H°$ for the desired equation.

Manipulating thermochemical equations (page 281)

Changing the direction of a reaction changes the sign of $\Delta H°$. When the coefficients are multiplied by a factor, the value of $\Delta H°$ is multiplied by the same factor. Formulas can be canceled only when the substances are in the same physical state. These rules are used in applying Hess's law.

Hess's law equation (page 287)

We use this equation with standard heats of formation, ΔH_f°, to calculate $\Delta H°$ for some desired equation.

$$\Delta H^\circ_{\text{reaction}} = [\text{sum of } \Delta H_f^\circ \text{ of all of the products}] - [\text{sum of } \Delta H_f^\circ \text{ of all of the reactants}]$$

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Kinetic and Potential Energy

7.1 Give definitions for **(a)** energy and **(b)** work.

7.2 Define **(a)** *kinetic energy* and **(b)** *potential energy.*

7.3 State the equation used to calculate an object's kinetic energy. Define the symbols used in the equation.

7.4 State the *law of conservation of energy*. Describe how it explains the motion of a child on a swing.

7.5 If a car increases its speed from 30 mph to 60 mph, by what factor does the kinetic energy of the car increase? If the mass of a truck is doubled—for example, when it is loaded—by what factor does the kinetic energy of the truck increase?

7.6 What is meant by the term *chemical energy*?

7.7 How does the potential energy change (increase, decrease, or no change) for each of the following?

(a) Two electrons come closer together.

(b) An electron and a proton become farther apart.

(c) Two atomic nuclei approach each other.

(d) A ball rolls downhill.

7.8 Define *heat*. How do *heat* and *temperature* differ?

7.9 On a molecular level, how is thermal equilibrium achieved when a hot object is placed in contact with a cold object?

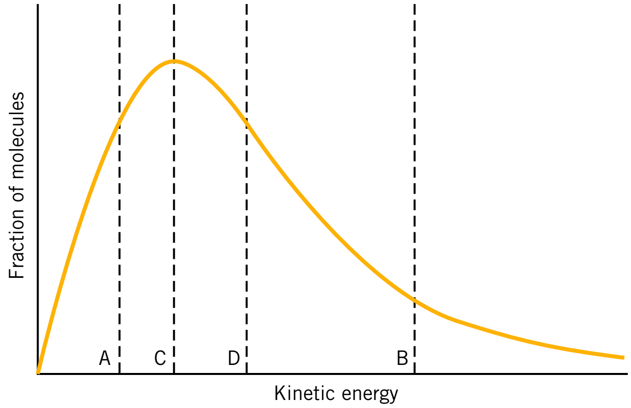
7.10 What is the SI unit of energy? How much energy (in joules and in calories) does a 75 kg object have if it's moving at 45 m s^{-1}?

7.11 Why is heat considered a waste product in a car engine?

Internal Energy and the Kinetic Theory of Matter

7.12 How is internal energy related to molecular kinetic and potential energy? How is a *change* in internal energy defined for a chemical reaction?

7.13 Consider the distribution of molecular kinetic energies shown in the following diagram for a gas at 25 °C:



(a) Which point corresponds to the most frequently occurring (also called the most probable) molecular kinetic energy?

(b) Which point corresponds to the average molecular kinetic energy?

(c) If the temperature of the gas is raised to 50 °C, how will the height of the curve at B change?

(d) If the temperature of the gas is raised to 50 °C, how will the height of the curve at A change? How will the maximum height of the curve change?

7.14 Suppose the temperature of an object is raised from 100 °C to 200 °C by heating it with a Bunsen burner. Which of the following will be true?

(a) The average molecular kinetic energy will increase.

(b) The total kinetic energy of all the molecules will increase.

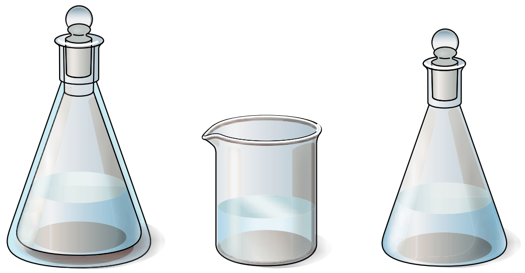
(c) The number of fast-moving molecules will increase.

(d) The number of slow-moving molecules will increase.

(e) The chemical potential energy will decrease.

7.15 A quart of boiling water will cause a more severe burn if it's spilled on you than just a drop of boiling water. Explain this in terms of the amounts of kinetic energy possessed by the water molecules in the two samples.

7.16 Consider the three systems depicted in the following drawing:



Label them as isolated, closed, and open. What are the differences between the three types of systems?

7.17 How can the *state* of a system be specified? What is a *state function*?

Experimental Measurement of Heat

7.18 What do the terms *system* and *surroundings* mean? What is the difference between an isolated system and a closed system? What is the universe in terms of thermodynamics?

7.19 What is the name of the thermal property whose values can have the following units?

(a) J g^{-1} $°C^{-1}$ **(b)** J mol^{-1} $°C^{-1}$ **(c)** J $°C^{-1}$

7.20 For samples with the same mass, which kind of substance needs more energy to undergo an increase of 5 °C, something with a *large* specific heat or something with a *small* specific heat? Explain.

7.21 How do heat capacity and specific heat differ?

7.22 What is the meaning of a negative value for q?

7.23 Suppose object A has twice the specific heat and twice the mass of object B. If the same amount of heat is applied to both objects, how will the temperature change of A be related to the temperature change in B?

Energy Changes in Chemical Reactions

7.24 In a certain chemical reaction, there is a decrease in the potential energy (chemical energy) as the reaction proceeds.

(a) How does the total kinetic energy of the particles change?

(b) How does the temperature of the reaction mixture change?

7.25 What term do we use to describe a reaction that liberates heat to its surroundings? How does the chemical energy change during such a reaction? What is the algebraic sign of q for such a reaction?

7.26 What term is used to describe a reaction that absorbs heat from the surroundings? How does the chemical energy change during such a reaction? What is the algebraic sign of q for such a reaction?

7.27 When gasoline burns, it reacts with oxygen in the air and forms hot gases consisting of carbon dioxide and water vapor. How does the potential energy of the gasoline and oxygen compare with the potential energy of the carbon dioxide and water vapor?

Internal Energy and Enthalpy

7.28 Write the equation that states the first law of thermodynamics. In your own words, what does this statement mean in terms of energy exchanges between a system and its surroundings?

7.29 How is enthalpy defined?

7.30 What is the *sign* of ΔH for an endothermic change?

7.31 If the enthalpy of a system increases by 100 kJ, what must be true about the enthalpy of the surroundings? Why?

7.32 When we measure the heat of combustion of glucose, $C_6H_{12}O_6$, in a bomb calorimeter, what products are formed in the reaction? Is the heat we measure equal to ΔE or ΔH?

7.33 If a system containing gases expands and pushes back a piston against a constant opposing pressure, what equation describes the work done on the system?

7.34 Consider the reaction,

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$$

Are the values of ΔE and ΔH expected to be appreciably different?

Enthalpy and Heats of Reaction

7.35 Why do standard reference values for temperature and pressure have to be selected when we consider and compare heats of reaction for various reactions? What are the values for the standard temperature and standard pressure?

7.36 What distinguishes a *thermochemical* equation from an ordinary chemical equation?

7.37 Why are fractional coefficients permitted in a balanced thermochemical equation? If a formula in a thermochemical equation has a coefficient of $\frac{1}{2}$, what does it signify?

Hess's Law

7.38 What fundamental fact about ΔH makes Hess's law possible?

7.39 What *two* conditions must be met by a thermochemical equation so that its standard enthalpy change can be given the symbol ΔH_f°?

Review Problems

First Law of Thermodynamics

7.40 If a system does 45 J of work and receives 28 J of heat, what is the value of ΔE for this change?

7.41 If a system has 48 J of work done on it and absorbs 22 J of heat, what is the value of ΔE for this change?

7.42 An automobile engine converts heat into work via a cycle. The cycle must finish exactly where it started, so the energy at the start of the cycle must be exactly the same as the energy at the end of the cycle. If the engine is to do 100 J of work per cycle, how much heat must it absorb?

7.43 If a battery can release 535 J of energy and 455 J are used for work, how much energy is released as heat?

7.44 If the engine in Problem 7.42 absorbs 250 joules of heat per cycle, how much work can it do per cycle?

7.45 Chargers for cell phones get warm while they are being used. Some of the energy that they are using is being used to power the cell phone and the rest is wasted as heat. If a cell phone battery needs 235 J of energy and 345 J are wasted as heat, how many joules are required to charge the cell phone?

Thermal Properties, Measuring Energy Changes

7.46 How much heat, in joules and in calories, must be removed from 1.75 mol of water to lower its temperature from 25.0 to 15.0 °C?

7.47 How much heat, in joules and calories, is needed to heat up 215 mL of water from 25.0 °C to 99.0 °C?

OH **7.48** How many grams of water can be heated from 25.0 °C to 35.0 °C by the heat released from 85.0 g of iron that cools from 85.0 °C to 35.0 °C?

7.49 How many grams of copper can be cooled from 67.0 to 32.3 °C by the heat gained by 100.0 g of water that has an increase in temperature from 27.0 to 32.3 °C?

7.50 A 5.00 g mass of a metal was heated to 100.0 °C and then plunged into 100.0 g of water at 24.0 °C. The temperature of the resulting mixture became 28.0 °C.

(a) How many joules did the water absorb?

(b) How many joules did the metal lose?

(c) What is the heat capacity of the metal sample?

(d) What is the specific heat of the metal?

7.51 A sample of copper was heated to 120.00 °C and then thrust into 200.0 g of water at 25.00 °C. The temperature of the mixture became 26.50 °C.

(a) How much heat in joules was absorbed by the water?

(b) The copper sample lost how many joules?

(c) What was the mass in grams of the copper sample?

OH **7.52** Calculate the molar heat capacity of iron in J mol^{-1} $°C^{-1}$. Its specific heat is 0.4498 J g^{-1} $°C^{-1}$.

7.53 What is the molar heat capacity of ethyl alcohol, C_2H_5OH, in units of J mol^{-1} $°C^{-1}$, if its specific heat is 0.586 cal g^{-1} $°C^{-1}$?

7.54 A vat of 4.54 kg of water underwent a decrease in temperature from 60.25 to 58.65 °C. How much energy in kilojoules left the water? (For this range of temperature, use a value of 4.18 J g^{-1} $°C^{-1}$ for the specific heat of water.)

7.55 A container filled with 2.46 kg of water underwent a temperature change from 25.24 °C to 27.31 °C. How much heat, measured in kilojoules, did the water absorb?

Calorimetry

OH **7.56** Nitric acid neutralizes potassium hydroxide. To determine the heat of reaction, a student placed 55.0 mL of 1.3 *M* HNO_3 in a coffee cup calorimeter, noted that the temperature was 23.5 °C, and added 55.0 mL of 1.3 *M* KOH, also at 23.5 °C. The mixture was stirred quickly with a thermometer, and its temperature rose to 31.8 °C. Write the balanced equation for the reaction. Calculate the heat of reaction in joules. Assume that the specific heats of all solutions are 4.18 J g^{-1} $°C^{-1}$ and that all densities are 1.00 g mL^{-1}. Calculate the heat of reaction per mole of acid (in units of kJ mol^{-1}).

7.57 In the reaction between formic acid ($HCHO_2$) and sodium hydroxide, water and sodium formate ($NaCHO_2$) are formed. To determine the heat of reaction, 75.0 mL of 1.07 *M* $HCHO_2$ was placed in a coffee cup calorimeter at a temperature of 22.4 °C, and 45.0 mL of 1.78 *M* NaOH, also at 22.4 °C, was added. The mixture was stirred quickly with a thermometer, and its temperature rose to 23.4 °C. Write the balanced chemical equation for the reaction. Calculate the heat of reaction in joules. Assume that the specific heats of all solutions are 4.18 J g^{-1} $°C^{-1}$ and that all densities are 1.00 g mL^{-1}. Calculate the heat of reaction per mole of acid (in units of kJ mol^{-1}).

7.58 A 1.000 mol sample of propane, a gas used for cooking in many rural areas, was placed in a bomb calorimeter with excess oxygen and ignited. The initial temperature of the calorimeter was 25.000 °C and its total heat capacity was 97.13 kJ $°C^{-1}$. The reaction raised the temperature of the calorimeter to 27.282 °C.

(a) Write the balanced chemical equation for the reaction in the calorimeter.

(b) How many joules were liberated in this reaction?

(c) What is the heat of reaction of propane with oxygen expressed in kilojoules per mole of C_3H_8 burned?

7.59 Toluene, C_7H_8, is used in the manufacture of explosives such as TNT (trinitrotoluene). A 1.500 g sample of liquid toluene was placed in a bomb calorimeter along with excess oxygen. When the combustion of the toluene was initiated, the temperature of the calorimeter rose from 25.000 °C to 26.413 °C. The products of the combustion were $CO_2(g)$ and $H_2O(l)$, and the heat capacity of the calorimeter was 45.06 kJ $°C^{-1}$.

(a) Write the balanced chemical equation for the reaction in the calorimeter.

(b) How many joules were liberated by the reaction?

(c) How many joules would be liberated under similar conditions if 1.000 mol of toluene was burned?

Enthalpy Changes and Heats of Reaction

7.60 One thermochemical equation for the reaction of carbon monoxide with oxygen is

$$3CO(g) + \frac{3}{2}O_2(g) \longrightarrow 3CO_2(g) \quad \Delta H° = -849 \text{ kJ}$$

(a) Write the thermochemical equation for the reaction using 2.00 mol of CO.

(b) What is $\Delta H°$ for the formation of 1.00 mol of CO_2 by this reaction?

OH **7.61** Ammonia reacts with oxygen as follows:

$$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g) \qquad \Delta H° = -1132 \text{ kJ}$$

(a) Calculate the enthalpy change for the combustion of 1.00 mol of NH_3.

(b) Write the thermochemical equation for the reaction in which one mole of H_2O is formed.

7.62 Magnesium burns in air to produce a bright light and is often used in fireworks displays. The combustion of magnesium can be described by the following thermochemical equation:

$$2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s) \qquad \Delta H^\circ = -1203 \text{ kJ}$$

How much heat (in kilojoules) is liberated by the combustion of 6.54 g of magnesium?

7.63 Methanol is the fuel in "canned heat" containers (e.g., Sterno) that are used to heat foods at cocktail parties. The combustion of methanol can be described by the following thermochemical equation:

$$2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \qquad \Delta H^\circ = -1199 \text{ kJ}$$

How many kilojoules are liberated by the combustion of 46.0 g of methanol?

7.64 Methane burns with oxygen to produce carbon dioxide and water as a gas. The balanced thermochemical equation is

$$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \qquad \Delta H^\circ = -802 \text{ kJ}$$

How much methane, in grams, must be burned to release 432 kJ of heat?

7.65 Methanol, as described in Problem 7.63, is used to heat food. The combustion of methanol can be described by the following thermochemical equation:

$$2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \qquad \Delta H^\circ = -1199 \text{ kJ}$$

How much methanol, in grams, is needed to release 625 kJ of heat?

Hess's Law

7.66 Construct an enthalpy diagram that shows the enthalpy changes for a one-step conversion of germanium, Ge(s), into GeO$_2$(s), the dioxide. On the same diagram, show the two-step process, first to the monoxide, GeO(s), and then its conversion to the dioxide. The relevant thermochemical equations are the following:

$$\text{Ge}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{GeO}(s) \qquad \Delta H^\circ = -255 \text{ kJ}$$

$$\text{Ge}(s) + \text{O}_2(g) \longrightarrow \text{GeO}_2(s) \qquad \Delta H^\circ = -534.7 \text{ kJ}$$

Using this diagram, determine ΔH° for the following reaction:

$$\text{GeO}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{GeO}_2(s)$$

7.67 Construct an enthalpy diagram for the formation of NO$_2$(g) from its elements by two pathways: first, from its elements and, second, by a two-step process, also from the elements. The relevant thermochemical equations are

$$\tfrac{1}{2}\text{N}_2(g) + \text{O}_2(g) \longrightarrow \text{NO}_2(g) \qquad \Delta H^\circ = +33.8 \text{ kJ}$$

$$\tfrac{1}{2}\text{N}_2(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}(g) \qquad \Delta H^\circ = +90.37 \text{ kJ}$$

$$\text{NO}(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}_2(g) \qquad \Delta H^\circ = ?$$

Be sure to note the signs of the values of ΔH° associated with arrows pointing up or down. Using the diagram, determine the value of ΔH° for the third equation.

7.68 Show how the equations

$$\text{N}_2\text{O}_4(g) \longrightarrow 2\text{NO}_2(g) \qquad \Delta H^\circ = +57.93 \text{ kJ}$$

$$2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g) \qquad \Delta H^\circ = -113.14 \text{ kJ}$$

can be manipulated to give ΔH° for the following reaction:

$$2\text{NO}(g) + \text{O}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$$

7.69 We can generate hydrogen chloride by heating a mixture of sulfuric acid and potassium chloride according to the equation

$$2\text{KCl}(s) + \text{H}_2\text{SO}_4(l) \longrightarrow 2\text{HCl}(g) + \text{K}_2\text{SO}_4(s)$$

Calculate ΔH° in kilojoules for this reaction from the following thermochemical equations:

$$\text{HCl}(g) + \text{KOH}(s) \longrightarrow \text{KCl}(s) + \text{H}_2\text{O}(l) \qquad \Delta H^\circ = -203.6 \text{ kJ}$$

$$\text{H}_2\text{SO}_4(l) + 2\text{KOH}(s) \longrightarrow \text{K}_2\text{SO}_4(s) + 2\text{H}_2\text{O}(l) \qquad \Delta H^\circ = -342.4 \text{ kJ}$$

7.70 Calculate ΔH° in kilojoules for the following reaction, the preparation of the unstable acid nitrous acid, HNO$_2$.

$$\text{HCl}(g) + \text{NaNO}_2(s) \longrightarrow \text{HNO}_2(l) + \text{NaCl}(s)$$

Use the following thermochemical equations:

$$2\text{NaCl}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{HCl}(g) + \text{Na}_2\text{O}(s) \qquad \Delta H^\circ = +507.31 \text{ kJ}$$

$$\text{NO}(g) + \text{NO}_2(g) + \text{Na}_2\text{O}(s) \longrightarrow 2\text{NaNO}_2(s) \qquad \Delta H^\circ = -427.14 \text{ kJ}$$

$$\text{NO}(g) + \text{NO}_2(g) \longrightarrow \text{N}_2\text{O}(g) + \text{O}_2(g) \qquad \Delta H^\circ = -42.68 \text{ kJ}$$

$$2\text{HNO}_2(l) \longrightarrow \text{N}_2\text{O}(g) + \text{O}_2(g) + \text{H}_2\text{O}(l) \qquad \Delta H^\circ = +34.35 \text{ kJ}$$

7.71 Calcium hydroxide reacts with hydrochloric acid by the following equation:

$$\text{Ca(OH)}_2(aq) + 2\text{HCl}(aq) \longrightarrow \text{CaCl}_2(aq) + 2\text{H}_2\text{O}(l)$$

Calculate ΔH° in kilojoules for this reaction, using the following equations as needed:

$$\text{CaO}(s) + 2\text{HCl}(aq) \longrightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) \qquad \Delta H^\circ = -186 \text{ kJ}$$

$$\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca(OH)}_2(s) \qquad \Delta H^\circ = -65.1 \text{ kJ}$$

$$\text{Ca(OH)}_2(s) \xrightarrow[\text{dissolving in water}]{} \text{Ca(OH)}_2(aq) \qquad \Delta H^\circ = -12.6 \text{ kJ}$$

7.72 Given the following thermochemical equations,

$$CaO(s) + Cl_2(g) \longrightarrow CaOCl_2(s) \qquad \Delta H° = -110.9 \text{ kJ}$$

$$H_2O(l) + CaOCl_2(s) + 2NaBr(s) \longrightarrow 2NaCl(s) + Ca(OH)_2(s) + Br_2(l) \qquad \Delta H° = -60.2 \text{ kJ}$$

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l) \qquad \Delta H° = +65.1 \text{ kJ}$$

calculate the value of $\Delta H°$ (in kilojoules) for the reaction

$$\tfrac{1}{2}Cl_2(g) + NaBr(s) \longrightarrow NaCl(s) + \tfrac{1}{2}Br_2(l)$$

7.73 Given the following thermochemical equations,

$$2Cu(s) + S(s) \longrightarrow Cu_2S(s) \qquad \Delta H° = -79.5 \text{ kJ}$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H° = -297 \text{ kJ}$$

$$Cu_2S(s) + 2O_2(g) \longrightarrow 2CuO(s) + SO_2(g) \qquad \Delta H° = -527.5 \text{ kJ}$$

calculate the standard enthalpy of formation (in kilojoules per mole) of CuO(*s*).

7.74 Given the following thermochemical equations,

$$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g) \qquad \Delta H° = -1132 \text{ kJ}$$

$$6NO_2(g) + 8NH_3(g) \longrightarrow 7N_2(g) + 12H_2O(g) \qquad \Delta H° = -2740 \text{ kJ}$$

calculate the value of $\Delta H°$ (in kilojoules) for the reaction

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$$

OH **7.75** Given the following thermochemical equations,

$$3Mg(s) + 2NH_3(g) \rightarrow Mg_3N_2(s) + 3H_2(g) \qquad \Delta H° = -371 \text{ kJ}$$

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightarrow NH_3(g) \qquad \Delta H° = -46 \text{ kJ}$$

calculate $\Delta H°$ (in kilojoules) for the following reaction:

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Hess's Law and Standard Heats of Formation

7.76 Which of the following thermochemical equations can have $\Delta H_f°$ for the heat of the reaction? If it cannot, then why not?

(a) $CO(NH_2)_2(aq) \longrightarrow CO(NH_2)_2(s)$

(b) $C + O + 2N + 4H \longrightarrow CO(NH_2)_2(aq)$

(c) $C(s, \text{graphite}) + \tfrac{1}{2}O_2(g) + N_2(g) + 4H_2(g) \longrightarrow CO(NH_2)_2(aq)$

(d) $2C(s, \text{graphite}) + O_2(g) + 2N_2(g) + 8H_2(g) \longrightarrow 2CO(NH_2)_2(aq)$

7.77 Which of the following thermochemical equations can have $\Delta H_f°$ for the heat of the reaction? If it cannot, then why not?

(a) $Na_2SO_4(s) + HCl(g) \longrightarrow H_2SO_4(l) + 2NaCl(s)$

(b) $H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l)$

(c) $2H + S + 4O + 4H \longrightarrow H_2SO_4(l)$

(d) $\tfrac{1}{2}H_2(g) + \tfrac{1}{2}S(s) + O_2(g) \longrightarrow \tfrac{1}{2}H_2SO_4(l)$

7.78 Write the thermochemical equations, including values of $\Delta H_f°$ in kilojoules per mole (from Table 7.2), for the formation of each of the following compounds from their elements, with everything in standard states.

(a) $HC_2H_3O_2(l)$, acetic acid

(b) $C_2H_5OH(l)$, ethyl alcohol

(c) $CaSO_4 \cdot 2H_2O(s)$, gypsum

(d) $Na_2SO_4(s)$, sodium sulfate

7.79 Write the thermochemical equations, including values of $\Delta H_f°$ in kilojoules per mole (from Appendix C), for the formation of each of the following compounds from their elements, with everything in standard states.

(a) $MgCl_2 \cdot 2H_2O(s)$

(b) $(NH_4)_2Cr_2O_7(s)$

(c) $POCl_3(g)$

(d) $CO(NH_2)_2(s)$

7.80 Using data in Table 7.2, calculate $\Delta H°$ in kilojoules for the following reactions.

(a) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$

(b) $HCl(g) + NaOH(s) \longrightarrow NaCl(s) + H_2O(l)$

7.81 Using data in Table 7.2, calculate $\Delta H°$ in kilojoules for the following reactions.

(a) $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$

(b) $2NH_3(g) + CO_2(g) \longrightarrow CO(NH_2)_2(s) + H_2O(l)$

7.82 The value for the standard heat of combustion, $\Delta H°_{\text{combustion}}$, for sucrose, $C_{12}H_{22}O_{11}$, is -5.65×10^3 kJ mol^{-1}. Write the thermochemical equation for the combustion of 1 mol of sucrose and calculate the value of $\Delta H_f°$ for this compound. The sole products of combustion are $CO_2(g)$ and $H_2O(l)$. Use data in Table 7.2 as necessary.

7.83 The thermochemical equation for the combustion of acetylene gas, $C_2H_2(g)$, is

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta H° = -2599.3 \text{ kJ}$$

Using data in Table 7.2, determine the value of $\Delta H_f°$ for acetylene gas.

Additional Problems

7.84 Look at the list of substances in Table 7.1. Which one will require the most energy to raise the temperature of a 50 g sample from 20 °C to 30 °C? Which substance will have the largest temperature increase if 40 kJ of heat was absorbed by 30 g of the substance?

7.85 A dilute solution of hydrochloric acid with a mass of 610.29 g and containing 0.33183 mol of HCl was exactly neutralized in a calorimeter by the sodium hydroxide in 615.31 g of a comparably dilute solution. The temperature increased from 16.784 to 20.610 °C. The specific heat of the HCl solution was 4.031 $J\ g^{-1}\ °C^{-1}$; that of the NaOH solution was 4.046 $J\ g^{-1}\ °C^{-1}$. The heat capacity of the calorimeter was 77.99 $J\ °C^{-1}$. Write the balanced equation for the reaction. Use the data above to calculate the heat evolved. What is the heat of neutralization per mole of HCl? Assume that the original solutions made independent contributions to the total heat capacity of the system following their mixing.

7.86 What is the kinetic energy of a helium atom moving at 1.23×10^3 m/s?

7.87 A 2.00 kg piece of granite with a specific heat of 0.803 $J\ g^{-1}\ °C^{-1}$ and a temperature of 95.0 °C is placed into 2.00 L of water at 22.0 °C. When the granite and water come to the same temperature, what will that temperature be?

7.88 In the recovery of iron from iron ore, the reduction of the ore is actually accomplished by reactions involving carbon monoxide. Use the following thermochemical equations,

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H° = -28\ kJ$$
$$3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g) \qquad \Delta H° = -59\ kJ$$
$$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g) \qquad \Delta H° = +38\ kJ$$

to calculate $\Delta H°$ for the reaction

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

7.89 Use the results of Problem 7.86 and the data in Table 7.2 to calculate the value of $\Delta H_f°$ for FeO. Express the answer in units of kilojoules per mole.

7.90 The amino acid glycine, $C_2H_5NO_2$, is one of the compounds used by the body to make proteins. The equation for its combustion is

$$4C_2H_5NO_2(s) + 9O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l) + 2N_2(g)$$

For each mole of glycine that burns, 973.49 kJ of heat is liberated. Use this information, plus values of $\Delta H_f°$ for the products of combustion, to calculate $\Delta H_f°$ for glycine.

7.91 The value of $\Delta H_f°$ for HBr(*g*) was first evaluated using the following standard enthalpy values obtained experimentally. Use these data to calculate the value of $\Delta H_f°$ for HBr(*g*).

$$Cl_2(g) + 2KBr(aq) \longrightarrow Br_2(aq) + 2KCl(aq) \qquad \Delta H° = -96.2\ kJ$$
$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H° = -184\ kJ$$
$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O(l) \qquad \Delta H° = -57.3\ kJ$$
$$HBr(aq) + KOH(aq) \longrightarrow KBr(aq) + H_2O(l) \qquad \Delta H° = -57.3\ kJ$$
$$HCl(g) \xrightarrow[\text{dissolving in water}]{} HCl(aq) \qquad \Delta H° = -77.0\ kJ$$
$$Br_2(g) \xrightarrow[\text{dissolving in water}]{} Br_2(aq) \qquad \Delta H° = -4.2\ kJ$$
$$HBr(g) \xrightarrow[\text{dissolving in water}]{} HBr(aq) \qquad \Delta H° = -79.9\ kJ$$

7.92 Acetylene, C_2H_2, is a gas commonly used in welding. It is formed in the reaction of calcium carbide, CaC_2, with water. Given the following thermochemical equations, calculate the value of $\Delta H_f°$ for acetylene in units of kilojoules per mole.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \qquad \Delta H° = -65.3\ kJ$$
$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g) \qquad \Delta H° = +462.3\ kJ$$
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H° = +178\ kJ$$
$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \qquad \Delta H° = -126\ kJ$$
$$2C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -220\ kJ$$
$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H° = +572\ kJ$$

OH **7.93** The reaction for the metabolism of sucrose, $C_{12}H_{22}O_{11}$, is the same as for its combustion in oxygen to yield $CO_2(g)$ and $H_2O(l)$. The standard heat of formation of sucrose is $-2230\ kJ\ mol^{-1}$. Use the data in Table 7.2 to compute the amount of energy (in kJ) released by metabolizing 1 oz (28.4 g) of sucrose.

7.94 Consider the following thermochemical equations:

$$(1)\ CH_3OH(l) + O_2(g) \longrightarrow HCHO_2(l) + H_2O(l) \qquad \Delta H° = -411\ kJ$$
$$(2)\ CO(g) + 2H_2(g) \longrightarrow CH_3OH(l) \qquad \Delta H° = -128\ kJ$$
$$(3)\ HCHO_2(l) \longrightarrow CO(g) + H_2O(l) \qquad \Delta H° = -33\ kJ$$

Suppose Equation (1) is reversed and divided by 2, Equations (2) and (3) are multiplied by $\frac{1}{2}$, and then the three adjusted equations are added. What is the net reaction, and what is the value of $\Delta H°$ for the net reaction?

7.95 Chlorofluoromethanes (CFMs) are carbon compounds of chlorine and fluorine and are also known as Freons. Examples are Freon-11 ($CFCl_3$) and Freon-12 (CF_2Cl_2), which have been used as aerosol propellants. Freons have also been used in refrigeration and air-conditioning systems. It is believed that as these Freons escape into the atmosphere, they lead to a significant depletion of ozone from the upper atmosphere where ozone protects the earth's inhabitants from harmful ultraviolet radiation. In the stratosphere CFMs absorb high-energy radiation from the sun and split off chlorine atoms that hasten the decomposition of ozone, O_3. Possible reactions are

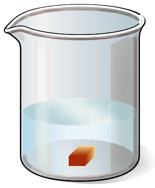
$$\begin{array}{ll}(1)\ O_3(g) + Cl(g) \longrightarrow O_2(g) + ClO(g) & \Delta H° = -126\ \text{kJ} \\ (2)\ ClO(g) + O(g) \longrightarrow Cl(g) + O_2(g) & \Delta H° = -268\ \text{kJ} \\ \hline (3)\ O_3(g) + O(g) \longrightarrow 2O_2(g) & \end{array}$$

The O atoms in Equation 2 come from the breaking apart of O_2 molecules caused by radiation from the sun. Use Equations 1 and 2 to calculate the value of $\Delta H°$ (in kilojoules) for Equation 3, the net reaction for the removal of O_3 from the atmosphere.

7.96 Suppose a truck with a mass of 14.0 tons (1 ton = 2000 lb) is traveling at a speed of 45.0 mi/hr. If the truck driver slams on the brakes, the kinetic energy of the truck is changed to heat as the brakes slow the truck to a stop. How much would the temperature of 5.00 gallons of water increase if all this heat could be absorbed by the water?

7.97 How much work must be done to form one mole of CH_4 and enough oxygen from CO_2 and H_2O? Why is it so difficult to carry out this reaction?

7.98 A cold (0.50 °C) piece of copper (5.25 g) was placed into a beaker with 50 mL of water at 32.4 °C.



(a) Draw an arrow showing the flow of heat.

(b) What is the sign of q for the water? What is the sign of q for the copper?

(c) What is the final temperature of the system?

7.99 Both Na_2CO_3 and $NaHCO_3$ can be used to neutralize acids. Using the information from Appendix C, which base gives off the most heat in neutralizing 1 mole of hydrochloric acid?

***7.100** When 4.56 g of a solid mixture composed of NH_4Cl and $CaCl_2$ was dissolved in 100.0 mL water, the temperature of the water rose by 5.33 °C. How many grams of each substance was in the mixture?

Multi-Concept Problems

***7.101** For ethanol, C_2H_5OH, which is mixed with gasoline to make the fuel gasohol, $\Delta H_f° = -277.63$ kJ/mol. Calculate the number of kilojoules released when 1 gallon of ethanol is burned completely. The density of ethanol is 0.787 g cm^{-3}. Use the data in Table 7.2 to help in the computation.

7.102 Both calcium and potassium react with water to form hydrogen and the corresponding hydroxide. The potassium hydroxide is soluble in water but the calcium hydroxide is not. Calculate the heats of reaction for both the reaction of potassium with water and that of calcium with water. Considering the metal, on a per mole basis and a per gram basis, which reaction gives off more heat? How many electrons are transferred in each reaction? On a per mole of electron basis, which reaction gives off more heat?

7.103 As a routine safety procedure, acids and bases should be stored separately in a laboratory. Concentrated hydrochloric acid is 12.0 M and the molarity of 25% ammonium hydroxide is 13.4 M. Both are sold in 2.5 L bottles. If there were an accident and the two bottles broke and the acid and base mixed, how much heat would evolve?

$$NH_4OH(aq) + HCl(aq) \longrightarrow NH_4Cl(aq) + H_2O(l) \qquad \Delta H° = -50.49\ \text{kJ}$$

Exercises in Critical Thinking

7.104 Growing wheat and converting it into bread requires energy. In the process, the wheat absorbs sunlight and through photosynthesis converts carbon dioxide and water into carbohydrates. The plants are harvested and the wheat is ground into flour. The flour is transported to a bakery where it is baked into bread. The bread is sold and then consumed by the customer. After eating a piece of bread, the customer goes for a walk. What are the different forms of energy, and how is the energy converted from one form to another in these processes?

7.105 Suppose we compress a spring, tie it up tightly, and then dissolve the spring in acid. What happens to the potential energy contained in the compressed spring? How could you measure it?

7.106 Carefully and precisely describe the difference between H, ΔH, and $\Delta H°$.

7.107 Why do we usually use $\Delta H°$ rather than $\Delta E°$ when we discuss energies of reaction? Develop an argument for using $\Delta E°$ instead.

7.108 Explain why we can never determine values for E or H. Make a list of the factors we would need to know to determine E or H.

7.109 Find the heats of formation of some compounds that are explosives. What do they have in common? Compare them to the $\Delta H_f°$ values of stable compounds such as H_2O, NaCl, and $CaCO_3$. Formulate a generalization to summarize your observations.

7.110 A 100 g piece of granite and a 100 g piece of lead are placed in an oven that is at 100 °C. The initial temperatures of the pieces are 25 °C. After a couple of minutes, neither one is at 100 °C, but which one is warmer? Which one will reach 100 °C first? How much energy will it take for both of the objects to reach 100 °C?

Chapters 5–7

[Bringing It Together]

Once again we pause to provide you an opportunity to see how well you have grasped the concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–4. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. How many molecules of $(CH_3)_2NH$ are needed to react completely with 2.00 mg of $H_2C_2O_4$?

2. Write a chemical equation showing the reaction of formic acid, $HCHO_2$, with water.

3. Write molecular, ionic, and net ionic equations for the reaction that occurs when a solution of formic acid is added to a solution of methylamine, CH_3NH_2. Explain what happens to the electrical conductivity of the solution during the addition.

4. Methylamine, CH_3NH_2, is a weak base. Write a chemical equation showing its reaction with water.

5. Write molecular, ionic, and net ionic equations for the reaction that occurs when a solution containing hydrochloric acid is added to a solution of the weak base, methylamine (CH_3NH_2).

6. Write molecular, ionic, and net ionic equations for any reactions that would occur between the following pairs of compounds. If no reaction, write "N.R."

(a) $CuCl_2(aq)$ and $(NH_4)_2CO_3(aq)$
(b) $HCl(aq)$ and $MgCO_3(s)$
(c) $ZnCl_2(aq)$ and $AgC_2H_3O_2(aq)$
(d) $HClO_4(aq)$ and $NaCHO_2(aq)$
(e) $MnO(s)$ and $H_2SO_4(aq)$
(f) $FeS(s)$ and $HCl(aq)$

7. Write a chemical equation for the complete neutralization of phosphoric acid by sodium hydroxide.

8. Which of the following oxides are acidic and which are basic: P_4O_6, Na_2O, SeO_3, CaO, PbO, SO_2?

9. Write the formulas and names of all of the salts that could be formed by the reaction of the following acids with potassium hydroxide: (a) H_2SO_3, (b) nitric acid, (c) $HBrO_2$, (d) phosphoric acid, (e) carbonic acid.

10. An 84.3 mg sample of a diprotic acid composed only of carbon, hydrogen, and oxygen was dissolved in water and titrated with 52.7 mM (millimolar) NaOH. The titration required 21.31 mL for complete neutralization of the acid. A separate portion of the acid weighing 725.0 mg was burned in pure oxygen to give 850.4 mg of CO_2 and 261.1 mg H_2O. What is the molecular formula of the acid?

11. How many milliliters of 0.200 M barium chloride must be added to 27.0 mL of 0.600 M sodium sulfate to give a complete reaction between their solutes?

12. To neutralize the acid in 10.0 mL of 18.0 M H_2SO_4 that was accidentally spilled on a laboratory bench top, solid sodium bicarbonate was used. The container of sodium bicarbonate was known to weigh 155.0 g before this use, and out of curiosity its mass was measured as 144.5 g afterward. Was sufficient sodium bicarbonate used? Determine the limiting reactant and calculate the maximum yield in grams of sodium sulfate.

13. What mass of magnesium hydroxide will be formed when 30.0 mL of 0.200 M magnesium chloride solution is mixed with 25.0 mL of 0.420 M sodium hydroxide solution? What will be the molar concentrations of the ions remaining in solution?

14. Methanethiol, CH_3SH, is a foul-smelling gas produced in the intestinal tract by bacteria acting on albumin in the absence of air. If 4.28 g of CH_3SH are burned in an abundant supply of oxygen, what will be the total mass of the products of the reaction?

15. How many grams of 6.00 M HNO_3 with a density of 1.19 g cm^{-3} must be added to 200 mL of water to give 0.150 M HNO_3?

16. How many grams of CO_2 must be dissolved in 300 mL of 0.100 M Na_2CO_3 solution to change the solute entirely into $NaHCO_3$?

17. One way to prepare iodine is to react sodium iodate, $NaIO_3$, with hydroiodic acid, HI. The following reaction occurs.

$$NaIO_3 + 6HI \longrightarrow 3I_2 + NaI + 3H_2O$$

Calculate the number of moles and the number of grams of iodine that can be made this way from 16.4 g of $NaIO_3$.

18. The combustion of methane (the chief component of natural gas) follows the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$\Delta H°$ for this reaction is -802.3 kJ. How many grams of methane must be burned to provide enough heat to raise the temperature of 250 mL of water from 25.0 °C to 50.0 °C?

19. A certain toilet cleaner uses $NaHSO_4$ as its active ingredient. In an analysis, 0.500 g of the cleaner was dissolved in 30.0 mL of distilled water and required 24.60 mL of 0.105 M NaOH for complete neutralization in a titration. The net ionic equation for the reaction is

$$HSO_4^- + OH^- \longrightarrow H_2O + SO_4^{2-}$$

What was the percentage by weight of $NaHSO_4$ in the cleaner?

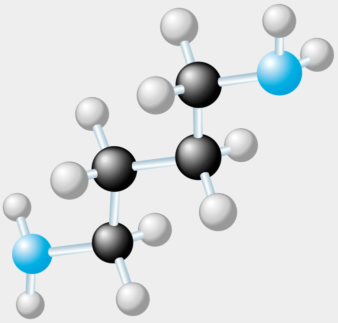
20. When 0.6484 g of cetyl palmitate, $C_{32}H_{64}O_2$ (a fruit wax), was burned in a bomb calorimeter with a heat capacity of 11.99 kJ/°C, the temperature of the calorimeter rose from 24.518 °C to 26.746 °C. Calculate the molar heat of combustion of cetyl palmitate in kJ/mol.

21. A white solid was known to be the anhydrous form of either sodium carbonate or sodium bicarbonate. Both react with hydrochloric acid to give sodium chloride, water, and carbon dioxide, but the mole proportions are not the same.

(a) Write the balanced equation for each reaction.

(b) It was found that 0.5128 g of the solid reacted with 47.80 mL of 0.2024 M HCl, and that the addition of more acid caused the formation of no more carbon dioxide. Perform the calculations that establish the identity of the unknown solid.

22. Putrescine, a foul smelling substance produced by rotting flesh, has the chemical structure shown below. How many milliliters of 0.166 *M* HCl are required to react completely with 1.07 g of this compound?



23. A sample of 10.1 g of ammonium nitrate was dissolved in 125 g of water in a coffee cup calorimeter. The temperature changed from 24.5 °C to 18.8 °C. Calculate the *heat of solution* of ammonium nitrate in kJ/mol. Assume that the energy exchange involves only the solution and that the specific heat of the solution is 4.18 J/g °C.

24. A calorimeter vat in which a stirring motor, a thermometer, and a "bomb" are immersed absorbed the heat released by the combustion of 0.514 g of benzoic acid. The thermochemical equation for its combustion is as follows.

$$2C_7H_6O_2(s) + 15O_2(g) \longrightarrow 14CO_2(g) + 6H_2O(l) \qquad \Delta H° = -7048 \text{ kJ}$$

The temperature of the calorimeter rose from 24.112 °C to 24.866 °C. What is the heat capacity of this calorimeter in kJ/°C?

25. For the following unbalanced equations, write the reactants and products in the form they should appear in an ionic equation. Then write balanced net ionic equations by applying the ion–electron method.

(a) $K_2Cr_2O_7 + HCl \longrightarrow KCl + Cl_2 + H_2O + CrCl_3$

(b) $KOH + SO_2 + KMnO_4 \longrightarrow K_2SO_4 + MnO_2 + H_2O$

26. The standard heat of combustion of eicosane, $C_{20}H_{42}(s)$, a typical component of candle wax, is 1.332×10^4 kJ/mol when it burns in pure oxygen and the products are cooled to 25 °C. The only products are $CO_2(g)$ and $H_2O(l)$. Calculate the value of the standard heat of formation of eicosane (in kJ/mol) and write the corresponding thermochemical equation.

27. Calculate the standard heat of formation of calcium carbide, $CaC_2(s)$, in kJ/mol using the following thermochemical equations.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + H_2(g) \qquad \Delta H° = -414.79 \text{ kJ}$$

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \qquad \Delta H° = -221.0 \text{ kJ}$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \qquad \Delta H° = -65.19 \text{ kJ}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H° = -571.8 \text{ kJ}$$

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g) \qquad \Delta H° = +462.3 \text{ kJ}$$

28. Complete and balance the following equations if a reaction occurs.

(a) $Sn(s) + HCl(aq) \longrightarrow$

(b) $Cu(s) + HNO_3(\text{conc.}) \longrightarrow$

(c) $Zn(s) + Cu^{2+}(aq) \longrightarrow$

(d) $Ag(s) + Cu^{2+}(aq) \longrightarrow$

29. *Bordeaux mixture* is traditionally prepared by mixing copper(II) sulfate and calcium hydroxide in water. The resulting suspension of copper(II) hydroxide is sprayed on trees and shrubs to fight fungus diseases. This fungicide is also available in commercial preparations. In an analysis of one such product, a sample weighing 0.238 g was dissolved in hydrochloric acid. Excess KI solution was then added, forming CuI and I_2, and the iodine that was formed was titrated with 0.01669 *M* $Na_2S_2O_3$ solution using starch as an indicator giving I^- and SO_4^{2-} as products. The titration required 28.62 mL of the thiosulfate solution. What was the percentage by weight of copper in the sample of Bordeaux mixture?

30. Suppose 237 mL of 0.556 *M* HCl is added to 622 mL of 1.05 *M* HCl. What is the molarity of the HCl in the final mixture?

31. The density of concentrated phosphoric acid solution is 1.689 g solution/mL solution at 20 °C. It contains 144 g of phosphoric acid per 1.00×10^2 mL of solution.

(a) Calculate the molar concentration of phosphoric acid in this solution.

(b) Calculate the number of grams of this solution required to contain 50.0 g phosphoric acid.

32. A mixture consists of lithium carbonate (Li_2CO_3) and potassium carbonate (K_2CO_3). These react with hydrochloric acid as follows.

$$Li_2CO_3(s) + 2HCl(aq) \longrightarrow 2LiCl(aq) + H_2O + CO_2(g)$$

$$K_2CO_3(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + H_2O + CO_2(g)$$

When 4.43 g of this mixture was analyzed, it consumed 53.2 mL of 1.48 *M* HCl. Calculate the number of grams of each carbonate and their percentages.

33. Write a balanced chemical equation for the combustion of cetane, $C_{16}H_{34}$, a hydrocarbon present in diesel fuel, (a) in the presence of excess oxygen, (b) in a somewhat limited supply of oxygen, and (c) in a severely limited supply of oxygen.

8 The Quantum Mechanical Atom

Chapter Outline

8.1 | Electromagnetic Radiation

8.2 | Line Spectra and the Rydberg Equation

8.3 | The Bohr Theory

8.4 | The Wave Mechanical Model

8.5 | Quantum Numbers of Electrons in Atoms

8.6 | Electron Spin

8.7 | Energy Levels and Ground State Electron Configurations

8.8 | Periodic Table and Ground State Electron Configurations

8.9 | Atomic Orbitals: Shapes and Orientations

8.10 | Periodic Table and Properties of the Elements

planet hollywood
TRADER VIC'S

The "strip" of Las Vegas is world famous for its dazzling array of lighted signs and creative displays of all shapes and colors. Behind these displays are the promise and excitement of many forms of entertainment. To chemists, these same lights and colors revolutionized physics and chemistry in the last century, while, importantly, providing a window into the structure of the atom itself. Tim Gartside USA/Alamy

This Chapter in Context

In previous chapters we have described how the existence and basic structure of atoms were deduced from a variety of experiments. However, there were many unanswered questions about the elements. Why do metals tend to form cations and why do nonmetals tend to form anions? Why do nonmetals combine to form molecules, while molecules made of metals are very rare? Why are the noble gases virtually inert? Why does the periodic table have the arrangement and shape it has? Many more questions could also be posed, but they are minor compared to major problems that were becoming apparent in the classical physics of the late 1800s and early 1900s.

■ When experiment and theory do not agree, the theory must be modified or discarded. Classical physics could not resolve the collapsing atom paradox. It also could not correctly predict the crucial characteristics of the radiation emitted by hot objects or hot samples of the elements.

First, classical physics, the physics of the late 1800s, predicted that atoms simply could not exist. It predicted that electrons must quickly lose energy and collapse into the nucleus—the *collapsing atom paradox*. Classical physics also predicted that heated objects should emit vast quantities of ultraviolet light. That they emit very little UV radiation led physicists to call this the *ultraviolet catastrophe*. Finally, particles, such as electrons, passing through very small openings gave results that could be explained only if we regarded particles as waves leading to the concept of the **wave/particle duality** of matter. These problems in describing the fundamental nature of matter made it clear that an entirely new set of theoretical concepts was needed. These concepts are commonly embodied in **quantum mechanics** (also called **wave mechanics** or **quantum theory**), which is now the cornerstone of modern chemistry.

8.1 | Electromagnetic Radiation

The Nature of Light

■ Like shaking a birthday present to try to guess its contents, scientists can “shake up” an atom by adding energy. Instead of hearing the rattle of a present, light is emitted. The energy and intensity of the light emitted helps to describe the inner workings of the atom.

You’ve learned that objects can have energy in only two ways, as kinetic energy and as potential energy. You also learned that energy can be transferred between things, and in Chapter 7 our principal focus was on the transfer of heat. Energy can also be transferred between atoms and molecules in the form of light or electromagnetic radiation. As we will see in this chapter, light is a very important form of energy in chemistry since it allows us to delve into the structure of atoms and molecules and, in some cases, their reactions. For example, many chemical systems emit visible light as they react often by a process called chemiluminescence (see Figure 8.1).

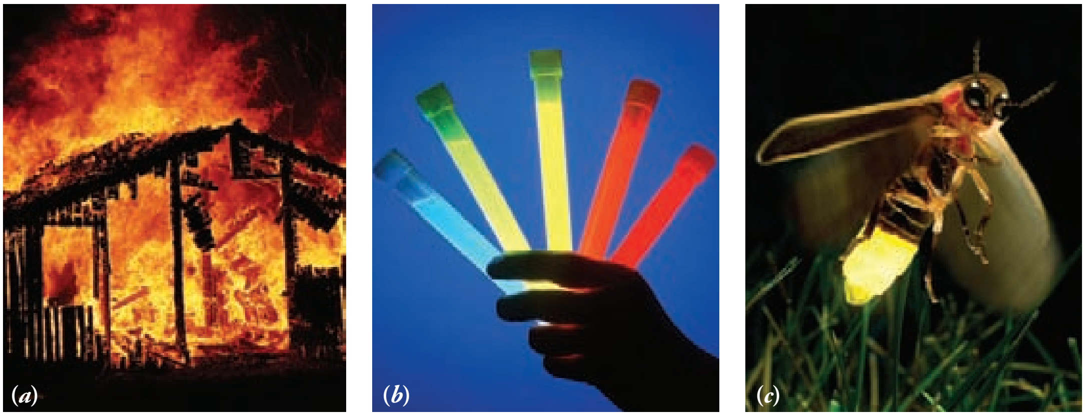


Figure 8.1 | **Light is given off in a variety of chemical reactions.** (*a*) Combustion. (*b*) Cyalume light sticks. (*c*) A lightning bug. *(Jim Richardson/Corbis, © Marc Steinmetz/Visum/The Image Works, © Phil Degginger/Alamy)*

Many experiments show that radiation carries energy through space by means of **waves**. Waves are an oscillation that moves outward from a disturbance (think of ripples moving away from a pebble dropped into a pond). In the case of **electromagnetic radiation**, the disturbance can be a pulsing, or oscillating, electric charge that creates an oscillating electric field. The oscillating electric field creates an oscillating magnetic field, and the two together are known as **electromagnetic waves**.

■ Electricity and magnetism are closely related to each other. A moving charge creates an electric current, which in turn creates a magnetic field around it. This is the fundamental idea behind electric motors. A moving magnetic field creates an electric field or current. This is also the idea behind electric generators and turbines.

Wavelength and Frequency

An electromagnetic wave is often depicted as a sine wave that has an amplitude, wavelength, and frequency (for simplicity we do not show the magnetic component of the wave). Figure 8.2 shows how the amplitude or intensity of the wave varies with time and with distance as the wave travels through space. The **amplitude** of the wave is related to the intensity or brightness of the radiation. In Figure 8.2*a*, we see two complete oscillations or *cycles* of the wave during a one-second interval. The number of cycles per second is called the **frequency** of the electromagnetic radiation, and its symbol is ν, the Greek letter nu. In the SI, the unit of time is the second (s), so frequency is given the unit "per second," which is $\frac{1}{\text{second}}$, or second^{-1}. This unit is given the special name **hertz (Hz)**.

$$1 \text{ Hz} = 1 \text{ s}^{-1}$$

■ Electromagnetic waves don't need a medium to travel through, as water and sound waves do. They can cross empty space. The speed of the electromagnetic wave in a vacuum is the same, about 3.00×10^8 m/s, no matter how the radiation is created.

■ ν, the symbol for frequency, is the Greek letter nu, pronounced "new."

■ The SI symbol for the second is s.

$$\text{s}^{-1} = \frac{1}{\text{s}}$$

As electromagnetic radiation moves away from its source, the positions of maximum and minimum amplitude (peaks and troughs) are regularly spaced. The peak-to-peak distance is called the radiation's **wavelength**, symbolized by λ (the Greek letter *lambda).* See Figure 8.2*b*. Because wavelength is a distance, it has distance units (for example, meters).

If we multiply the wavelength by frequency, the result is the velocity of the wave. We can see this if we analyze the units.

$$\text{meters} \times \frac{1}{\text{second}} = \frac{\text{meters}}{\text{second}} = \text{velocity}$$

$$\text{m} \times \frac{1}{\text{s}} = \frac{\text{m}}{\text{s}} = \text{m s}^{-1}$$

The velocity of electromagnetic radiation in a vacuum is a constant and is commonly called the *speed of light*. Its value to three significant figures is 3.00×10^8 m s^{-1}. This important physical constant is given the symbol c.

$$c = 3.00 \times 10^8 \text{ m s}^{-1}$$

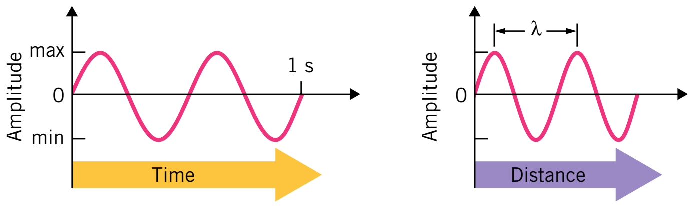
■ The speed of light is one of our most carefully measured constants because it is used to define the meter. The precise value of the speed of light in a vacuum is 2.99792458×10^8 m/s, and a meter is defined as exactly the distance traveled by light in 1/299792458 of a second.

From the preceding discussion we obtain a very important relationship that allows us to convert between λ and ν.

$$\lambda \times \nu = c = 3.00 \times 10^8 \text{ m s}^{-1} \tag{8.1}$$

TOOLS

Wavelength–frequency relationship



(*a*) (*b*)

Figure 8.2 | **Two views of electromagnetic radiation.** (*a*) The frequency, ν, of a light wave is the number of complete oscillations each second. Here two cycles span a one-second time interval, so the frequency is 2 cycles per second, or 2 Hz. (*b*) Electromagnetic radiation frozen in time. This curve shows how the amplitude varies along the direction of travel. The distance between two peaks is the wavelength, λ, of the electromagnetic radiation.

Example 8.1
Calculating Frequency from Wavelength

Mycobacterium tuberculosis, the organism that causes tuberculosis, can be completely destroyed by irradiation with ultraviolet light with a wavelength of 254 nm. What is the frequency of this radiation?

Analysis: Our analysis includes the realization that this question is not a conversion as our stoichiometry problems were. This will require an equation to solve.

Assembling the Tools: The tool needed is expressed by Equation 8.1. When rearranged it becomes

$$\nu = \frac{c}{\lambda}$$

However, we must be very careful about the units, and may need to consult the table of SI prefixes in Chapter 2.

Solution: We substitute 3.00×10^8 m s^{-1} for c and 254 nm for λ, the wavelength. However, to cancel units correctly, we must convert the wavelength to meters. Recall that nm means nanometer and the prefix nano implies the factor "$\times\ 10^{-9}$."

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$$

Therefore, 254 nm equals 254×10^{-9} m. Substituting gives

$$\begin{aligned}\nu &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{254 \text{ nm}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} \\ &= 1.18 \times 10^{15} \text{ s}^{-1} \\ &= 1.18 \times 10^{15} \text{ Hz}\end{aligned}$$

Is the Answer Reasonable? One way to test whether our answer is correct is to see if the given wavelength, multiplied by our calculated frequency, gives us the speed of light. To estimate the answer we round the numbers to one or two significant figures so we can do the calculation without a calculator. Rounding 254 nm to 250×10^{-9} m and our answer to 1×10^{15} s^{-1} we calculate

$$(250 \times 10^{-9} \text{ m}) \times (1 \times 10^{15} \text{ s}^{-1}) = 250 \times 10^6 \text{ m s}^{-1} = 2.5 \times 10^8 \text{ m s}^{-1}$$

which is close to the actual speed of light, within one significant figure. Using the actual data and a calculator gives us the exact value for the speed of light.

Example 8.2
Calculating Wavelength from Frequency

Radio station WKXR is an AM radio station broadcasting from Asheboro, North Carolina, at a frequency of 1260 kHz. What is the wavelength of these radio waves expressed in meters?

Analysis: We use the same analysis as in Example 8.1.

Assembling the Tools: This question will use the same equation as Example 8.1. This time we solve for wavelength in meters, as asked for in the problem.

$$\lambda = \frac{c}{\nu}$$

Solution: Solving Equation 8.1 for the wavelength we first have to consider units. The frequency in kilohertz has two parts. The prefix kilo stands for 10^3 and hertz stands for s^{-1}. Making those substitutions, we write

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1260 \text{ kHz}} = \frac{3.00 \times 10^8 \text{ m} \cancel{\text{s}^{-1}}}{1260 \times 10^3 \cancel{\text{s}^{-1}}}$$

When we cancel the units in the last term and work out the mathematics, we find that the wavelength is 238 meters.

Is the Answer Reasonable? If this wavelength is correct, we should be able to multiply it by the original frequency (in Hz) and get the speed of light, as we did in the previous example. Another approach is to test our answer by dividing the speed of light by the wavelength to get back the frequency. Rounding to one significant figure, we get

$$\frac{3 \times 10^8 \ \cancel{\text{m}}/\text{s}}{2 \times 10^2 \ \cancel{\text{m}}} = 1.5 \times 10^6 \text{ Hz} = 1500 \text{ kHz}$$

which is reasonably close to the original frequency of 1260 kHz.

Practice Exercises

8.1 | Helium derives it name from the Latin name for the sun. Helium was discovered when spectroscopists found that the 588 nm wavelength (among others) was missing from the sun's spectrum. What is the frequency of this radiation? (*Hint:* Recall the metric prefixes so units will cancel correctly.)

8.2 | The most intense radiation emitted by the Earth has a wavelength of about 10.9 μm. What is the frequency of this radiation in hertz?

8.3 | Radio station KRED in Eureka, California, broadcasts electromagnetic radiation at a frequency of 92.3 MHz (megahertz). What is the wavelength of these radio waves, expressed in meters?

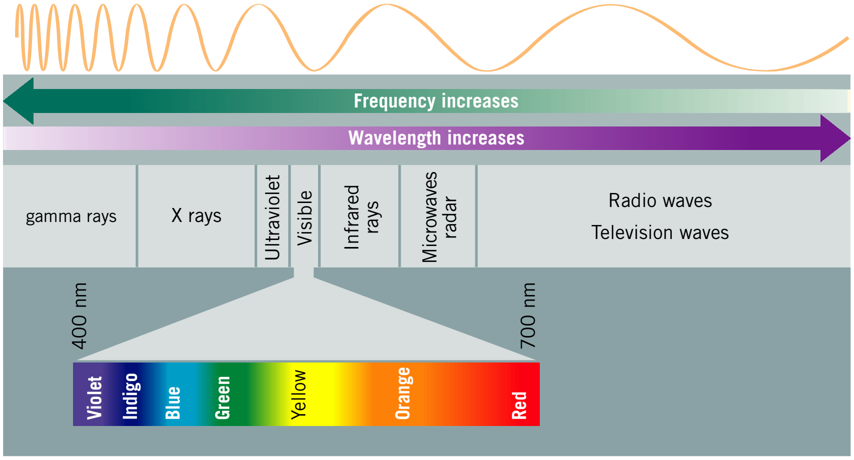
Electromagnetic Spectrum

Electromagnetic radiation comes in a broad range of frequencies called the **electromagnetic spectrum**, illustrated in Figure 8.3. Some portions of the spectrum have popular names. For example, radio waves are electromagnetic radiations having very low frequencies (and therefore very long wavelengths as we just calculated). Microwaves, which also have low frequencies, are emitted by radar instruments such as those the police use to monitor the speeds of cars. In microwave ovens, similar radiation is used to heat water in foods, causing the food to cook quickly. Infrared radiation is emitted by hot objects and consists of the range of frequencies that can make molecules of most substances vibrate internally. You can't see infrared radiation, but you can feel how your body absorbs it by holding your hand near a hot radiator; the absorbed radiation makes your hand warm. Gamma rays are at the high-frequency end of the electromagnetic spectrum. They are produced by certain elements that are radioactive. X rays are very much like gamma rays, but they are usually made by special equipment. Both X rays and gamma rays penetrate living things easily.

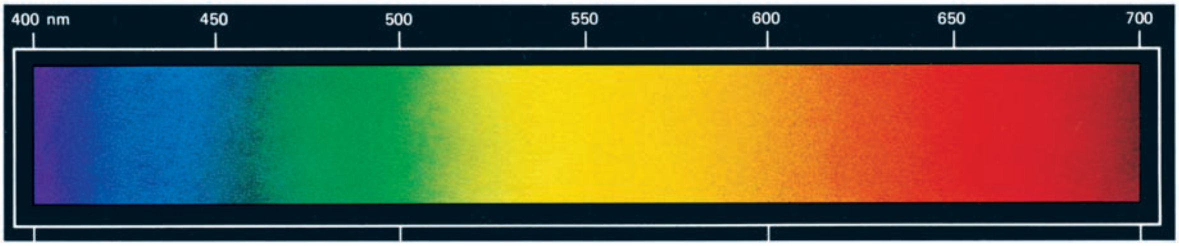
■ There is an inverse relationship between wavelength and frequency. The lower the frequency, the longer the wavelength.

Most of the time, you are bombarded with electromagnetic radiation from all portions of the electromagnetic spectrum, Figure 8.3*a*. Radio and TV signals pass through you; you feel infrared radiation when you sense the warmth of a radiator; X rays and gamma rays fall on you from space; and light from a lamp reflects into your eyes from the page you're reading. Of all these radiations, your eyes are able to sense only a very narrow band of wavelengths ranging from about 400 to 700 nm, Figure 8.3*b*. This band is called the **visible spectrum** and consists of all the colors you can see, from red through orange, yellow, green, blue, and violet. White light is composed of all these colors and can be separated into them by focusing a beam of

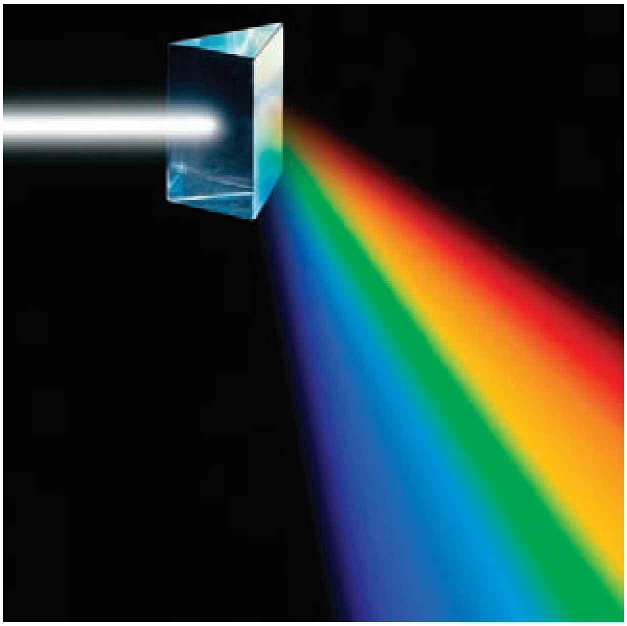
■ The speed of electromagnetic radiation was computed to be about 3×10^8 m/s. The fact that the same speed was determined experimentally for light supported the hypothesis that light was a form of electromagnetic radiation.


Frequency increases
Wavelength increases
gamma rays
X rays
Ultraviolet
Visible
Infrared rays
Microwaves radar
Radio waves
Television waves
400 nm
700 nm
Violet
Indigo
Blue
Green
Yellow
Orange
Red

(*a*)



(*b*)



(*c*)

Figure 8.3 | **The electromagnetic spectrum.** (*a*) The electromagnetic spectrum is divided into regions according to the wavelengths of the radiation. (*b*) The visible spectrum is composed of wavelengths that range from about 400 to 700 nm. (*c*) The production of a visible spectrum by splitting white light into its rainbow of colors.

white light through a prism, which spreads the various wavelengths apart. The visible spectrum is shown in Figure 8.3*b*. An illustration showing the production of a visible spectrum is given in Figure 8.3*c*.

The way substances absorb electromagnetic radiation often can help us characterize them. For example, each substance absorbs a uniquely different set of infrared frequencies. A plot of the intensities of absorption versus the wavelength is called an infrared absorption spectrum. It can be used to identify a compound, because each infrared spectrum is as unique as a set of fingerprints. (See Figure 8.4.) Many substances absorb visible and ultraviolet radiations in unique ways, too, and they have characteristic visible and ultraviolet absorption spectra (Figure 8.5).

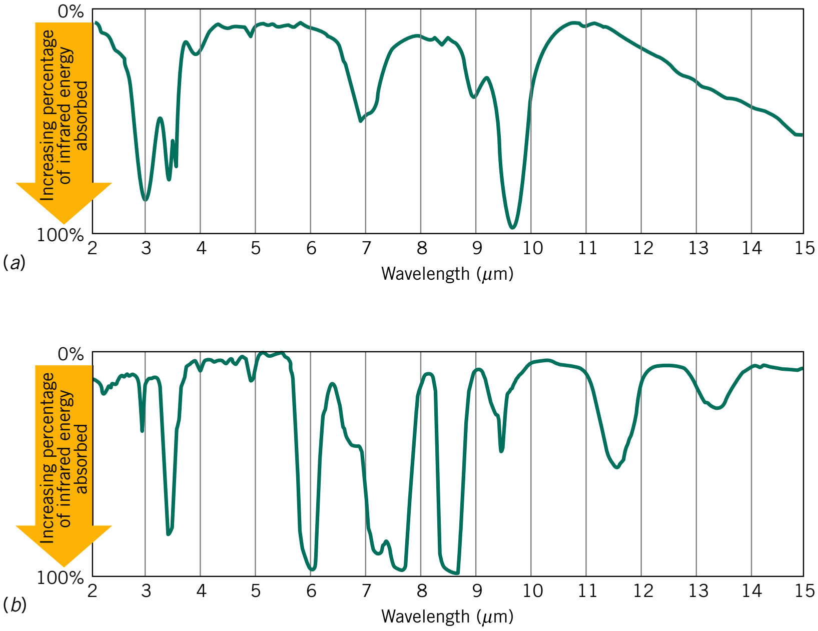


Figure 8.4 | **Absorption of infrared radiation by an organic compound.** (*a*) Infrared absorption spectrum of methanol. In an infrared spectrum, the usual practice is to show the amount of light absorbed increasing from top to bottom in the graph. Thus, for example, there is a peak in the percentage of light absorbed at about 3 μm. *(Spectrum courtesy Sadtler Research Laboratories, Inc., Philadelphia, Pa.).* (*b*) Infrared spectrum of acetone, which is found in nail polish remover mixed with water, fragrance, dyes, and sometimes moisturizers such as lanolin.

Light as a Stream of Photons

When an electromagnetic wave passes an object, the oscillating electric and magnetic fields may interact with it, as ocean waves interact with a buoy in a harbor. A tiny charged particle placed in the path of the wave will be yanked back and forth by the changing electric and magnetic fields. For example, when a radio wave strikes an antenna, electrons within the antenna begin to bounce up and down, creating an alternating current that can be detected and decoded electronically. Because the wave exerts a force on the antenna's electrons and moves them through a distance, work is done. Thus, as energy is lost by the source of the wave (the radio transmitter), energy is gained by the electrons in the antenna.

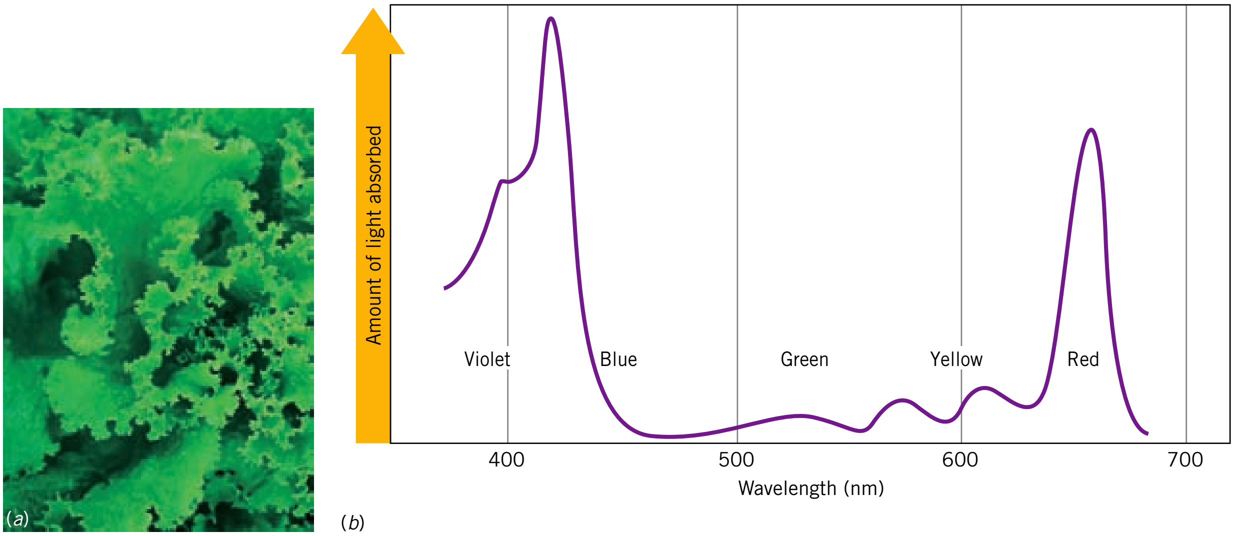


Figure 8.5 | **Absorption of light by chlorophyll.** (*a*) Chlorophyll is the green pigment plants use to harvest solar energy for photosynthesis. *(Gary Braasch/Riser/Getty)* (*b*) In this visible absorption spectrum of chlorophyll, the percentage of light absorbed increases from bottom to top. Thus, there is a peak in the light absorbed at about 420 nm and another at about 660 nm. This means the pigment strongly absorbs blue-violet and red light. The green color we *see* is the light that is *not* absorbed. It's composed of the wavelengths of visible light that are reflected. (Our eyes are most sensitive to green, so we don't notice the yellow components of the reflected light.)

Energy of a Photon

The energy of one photon is called one **quantum** of energy.

A series of groundbreaking experiments showed that classical physics does not correctly describe energy transfer by electromagnetic radiation. In 1900 a German physicist named Max Planck (1858–1947) proposed that electromagnetic radiation can be viewed as a stream of tiny packets or **quanta** of energy that were later called **photons.** Each photon travels at the speed of light. Planck proposed, and Albert Einstein (1879–1955) confirmed, that *the energy of a photon of electromagnetic radiation is proportional to the radiation's frequency,* not to its intensity or brightness as had been believed up to that time.

TOOLS

Energy of a photon

$$\text{Energy of a photon:} \qquad E = h\nu \tag{8.2}$$

The value of Planck's constant is 6.626×10^{-34} J s. It has units of energy (joules) multiplied by time (seconds).

In this expression, h is a proportionality constant that we now call **Planck's constant**. Note that Equation 8.2 relates two representations of electromagnetic radiation. The left-hand side of the equation deals with a property of particles (energy per photon); the right-hand side deals with a property of waves (the frequency). Quantum theory unites the two representations, so we can use whichever representation of electromagnetic radiation is convenient for describing experimental results.

Photoelectric Effect

One of the earliest clues to the relationship between the frequency of light and its energy was the discovery of the **photoelectric effect**. In the latter part of the nineteenth century, it was found that certain metals acquired a positive charge when they were illuminated by light. Apparently, light is capable of kicking electrons out of the surface of the metal.

When this phenomenon was studied in detail, it was discovered that electrons could only be made to leave a metal's surface if the frequency of the incident radiation was above some minimum value, which was named the threshold frequency. This threshold frequency differs for different metals, depending on how tightly the metal atom holds onto electrons. Above the threshold frequency, the kinetic energy of the emitted electron increases with increasing frequency of the light. Interestingly, however, its kinetic energy does not depend on the intensity of the light. In fact, if the frequency of the light is below the minimum frequency, no electrons are observed at all, no matter how bright the light is. To physicists of that time, this was very perplexing because they believed the energy of light was related to its brightness. The explanation of the phenomenon was finally given by Albert Einstein in the form of a very simple equation.

$$\text{KE} = h\nu - \text{BE}$$

where KE is the kinetic energy of the electron that is emitted, $h\nu$ is the energy of the photon, and BE is the minimum energy needed to eject the electron from the metal's surface (this can be considered the *binding energy*). Stated another way, part of the energy of the photon is needed just to get the electron off the surface of the metal, and this amount is BE. Any energy left over ($h\nu$ − BE) appears as the electron's kinetic energy.

Brighter light delivers more photons; higher frequency light delivers more energetic photons.

Analyzing and Solving Multi-Concept Problems

Using your microwave oven, how many moles of photons are needed to heat your cup of tea? Consider a cup of tea to be 237 mL of water starting at 25.0 °C and the drinking temperature to be a warm 85.5 °C. Also, most microwave ovens have Klystron tubes tuned to emit microwaves that are absorbed by water molecules at a wavelength of 12.24 cm.

Analysis This problem requires that we calculate the energy needed to heat a cup of tea. We can calculate the total energy needed using the tools presented in Chapter 7. Once we know the total energy, we can determine the number of photons from the tools presented in this section. Then we can use the information from Chapter 4 to calculate the moles of photons.

Strategy We have delineated three parts for this calculation: (1) calculate the total energy needed, (2) calculate the number of photons needed, and (3) convert the number of photons to moles of photons.

PART 1

Assembling the Tools To determine the energy needed to heat a cup of water, we need the calorimetry equation, Equation 7.7 on page 261, from Chapter 7.

$$\text{Heat energy (J)} = \text{(specific heat)(mass)(temperature change)}$$

Solution We know that the specific heat of water is 4.184 J g^{-1} $°C^{-1}$, and the mass is determined by converting 237 mL of water to 237 g of water using the density of water from Chapter 2. The change in temperature is 85.5 °C − 25.0 °C or 60.5 °C. Putting this together we get

$$\text{Heat energy (J)} = (4.184 \text{ J g}^{-1}\,°\text{C}^{-1})\,(237 \text{ g})\,(60.5\,°\text{C}) = 5.999 \times 10^4 \text{ J}$$

Notice that we will keep one extra significant figure until the final result is calculated.

PART 2

Assembling the Tools We can calculate the energy of one photon using Equation 8.2 combined with Equation 8.1 to get

$$E = \frac{hc}{\lambda}$$

Then we divide that into the total energy from Part 1 to determine the number of photons.

Solution The energy of one photon is

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cancel{\text{s}})\,(2.998 \times 10^{8} \ \cancel{\text{m}}\ \cancel{\text{s}^{-1}})}{(12.24 \times 10^{-2} \ \cancel{\text{m}})} = 1.623 \times 10^{-24} \text{ J photon}^{-1}$$

The number of photons is

$$\text{Number of photons} = \frac{(5.999 \times 10^{4} \ \cancel{\text{J}})}{(1.623 \times 10^{-24} \ \cancel{\text{J}} \text{ photon}^{-1})} = 3.696 \times 10^{28} \text{ photons}$$

PART 3

Assembling the Tools We use the tool for converting between elementary particles to moles, more commonly known as Avogadro's number.

$$1 \text{ mole photons} = 6.022 \times 10^{23} \text{ photons}$$

Solution We use our conversion factor to calculate moles from elementary units:

$$3.696 \times 10^{28} \ \cancel{\text{photons}} \left(\frac{1 \text{ mol photons}}{6.022 \times 10^{23} \ \cancel{\text{photons}}} \right) = 6.138 \times 10^{4} \text{ mol photons}$$

Correctly rounded the answer is 6.14 × 10^4 mol photons.

Is the Answer Reasonable? First of all, we expect that it will take a large number of photons to heat a cup of tea, and our answer supports that expectation. We then check our calculations, first by being sure that all units cancel and second by estimating the answers. For Part 1 we estimate the answer as 4 × 250 × 60 = 1000 × 60 = 60,000 which is very close to the 5.999 × 10^4 we got. For Part 2 the numerical part of the numbers is (6 × 3)/12 = 3/2. The exponential part of Part 2 is −34 + 8 −(−2) = −24. Our estimate is 1.5 × 10^{-24}, close to the answer we got. Similar estimates for the last two calculations also indicate that the math was done correctly.

The idea that electromagnetic radiation can be represented as either a stream of photons or a wave is a cornerstone of the quantum theory. Physicists were able to use this concept to understand many experimental results that classical physics simply could not explain. The success of the quantum theory in describing radiation paved the way for a second startling realization: that electrons, like radiation, could be represented as both waves and particles. We now turn our attention to the first experimental evidence that led to our modern quantum mechanical model of atomic structure: the existence of discrete lines in atomic spectra.

8.2 | Line Spectra and the Rydberg Equation

The spectrum described in Figure 8.3 is called a **continuous spectrum** because it contains a continuous unbroken distribution of light of *all* colors. It is formed when the light from an object that's been heated to a very high temperature (such as the filament in an electric light bulb), is split by a prism and displayed on a screen. A rainbow after a summer shower appears as a continuous spectrum that most people have seen. In this case, tiny water droplets in the air spread out the colors contained in sunlight.

A rather different kind of spectrum is observed if we examine the light that is given off when an *electric discharge*, or spark, passes through a gas such as hydrogen. The electric discharge is an electric current that *excites,* or energizes, the electrons in the atoms of the gas. When this occurs we say that an atom is in an **excited state**. The atoms then emit the absorbed energy in the form of light as the electrons return to a lower energy state. When a narrow beam of this light is passed through a prism, as shown in Figure 8.6, we do *not* see a continuous spectrum. Instead, only a few colors are observed, displayed as a series of individual lines. This series of lines is called the element's **atomic spectrum** or **emission spectrum**. Figure 8.7 shows the visible portions of the atomic spectra of two common elements, sodium and hydrogen, and how they compare with a continuous spectrum. Notice that the spectra of these elements are quite different. In fact, each element has its own unique atomic spectrum that is as characteristic as a fingerprint.

■ Atoms of an element can often be excited thermally by adding them to the flame of a Bunsen burner.

■ An emission spectrum is also called a ***line spectrum*** because the light corresponding to the individual emissions appear as lines on the screen.

Figure 8.6 | **Production and observation of an atomic spectrum.** Light emitted by excited atoms is formed into a narrow beam by the slits. It then passes through a prism, which divides the light into relatively few narrow beams with frequencies that are characteristic of the particular element that's emitting the light. When these beams fall on a screen, a series of lines is observed, which is why the spectrum is also called a line spectrum.

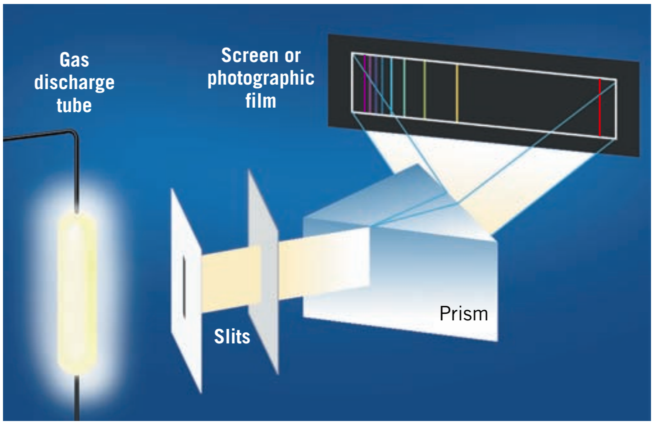
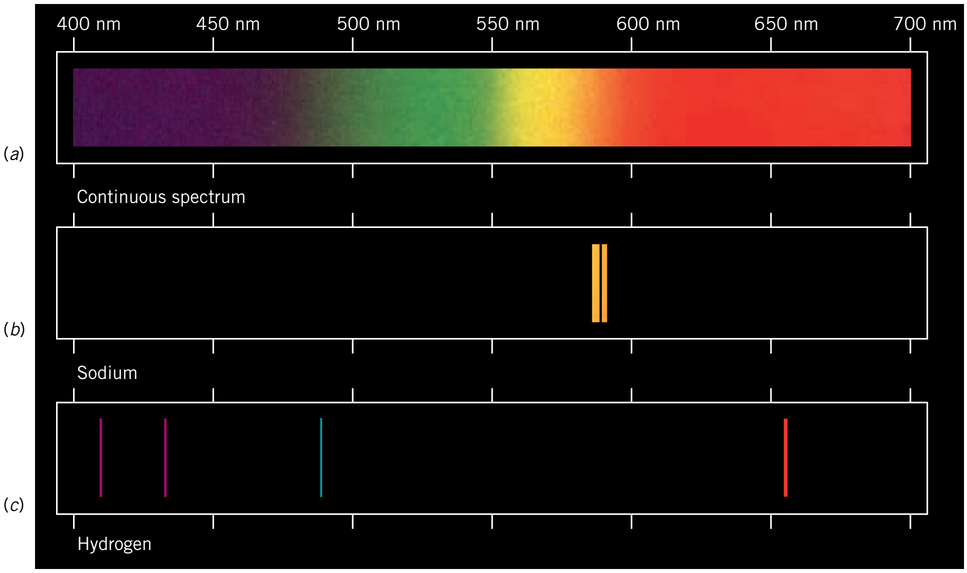


Figure 8.7 | **Continuous and atomic emission spectra.** (*a*) The continuous visible spectrum produced by the sun or an incandescent lamp. (*b*) The atomic emission spectrum produced by sodium. The emission spectrum of sodium actually contains more than 90 lines in the visible region. The two brightest lines are shown here. All the others are less than 1% as bright as these. (*c*) The atomic spectrum (line spectrum) produced by hydrogen. There are only four lines in this visible spectrum. They vary in brightness by only a factor of five, so they are all shown.



The Spectrum of Hydrogen

The first success in explaining atomic spectra quantitatively came with the study of the spectrum of hydrogen. This is the simplest element, because its atoms have only one electron, and it produces the simplest spectrum with the fewest lines.

The Rydberg Equation

The atomic spectrum of hydrogen actually consists of several series of lines. One series is in the visible region of the electromagnetic spectrum and is shown in Figure 8.7. A second series is in the ultraviolet region, and another is in the infrared. In 1885, J. J. Balmer found an equation that was able to give the wavelengths of the lines in the visible portion of the spectrum. This was soon extended to a more general equation, called the **Rydberg equation**, that could be used to calculate the wavelengths of *all* the spectral lines of hydrogen.

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

TOOLS

Rydberg equation

The symbol λ stands for the wavelength, R_H is a constant (109,678 cm^{-1}), and n_1 and n_2 are variables whose values are positive integers: 1, 2, 3 . . . . The only restriction is that the value of n_2 must be larger than n_1. (This ensures that the calculated wavelength has a positive value.) Thus, if $n_1 = 1$, acceptable values of n_2 are 2, 3, 4 . . . . The Rydberg constant, R_H, is an *empirical constant*, which means its value was chosen so that the equation gives values for λ that match the ones determined experimentally. The use of the Rydberg equation is straightforward, as illustrated in the following example.

Example 8.3

Calculating the Wavelength of a Line in the Hydrogen Spectrum

The lines in the visible portion of the hydrogen spectrum are called the Balmer series, for which $n_1 = 2$ in the Rydberg equation. Calculate, to four significant figures, the wavelength in nanometers of the spectral line in this series for which $n_2 = 4$.

Analysis: The wording of the question clearly indicates that the Rydberg equation will be used for this calculation.

Assembling the Tools: The Rydberg equation is given above. The values for n_1 and n_2 are clearly given and the only unknown left is the wavelength. We will also need the SI prefixes from Chapter 2.

Solution: To solve this problem, we substitute values into the Rydberg equation, which will give us $1/\lambda$. Substituting $n_1 = 2$ and $n_2 = 4$ into the Rydberg equation gives

$$\begin{aligned}\frac{1}{\lambda} &= 109{,}678\ \text{cm}^{-1}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\\ &= 109{,}678\ \text{cm}^{-1}\left(\frac{1}{4} - \frac{1}{16}\right)\\ &= 109{,}678\ \text{cm}^{-1}(0.25000 - 0.06250)\\ &= 109{,}678\ \text{cm}^{-1}(0.18750)\\ &= 2.05646 \times 10^4\ \text{cm}^{-1}\end{aligned}$$

Now that we have $\frac{1}{\lambda}$, taking the reciprocal gives the wavelength in centimeters.

$$\begin{aligned}\lambda &= \frac{1}{2.05646 \times 10^4\ \text{cm}^{-1}}\\ &= 4.86272 \times 10^{-5}\ \text{cm}\end{aligned}$$

Finally, we convert centimeters to nanometers.

$$\lambda = 4.86272 \times 10^{-5}\ \cancel{\text{cm}} \times \frac{10^{-2}\ \cancel{\text{m}}}{1\ \cancel{\text{cm}}} \times \frac{1\ \text{nm}}{10^{-9}\ \cancel{\text{m}}}$$

$$= 486.272\ \text{nm}$$

The answer rounded to four significant figures is 486.3 nm. Notice that the values for n are exact numbers, and we could have kept all six significant figures.

■ **Is the Answer Reasonable?** Besides double-checking the arithmetic, we can note that the wavelength falls within the visible region of the spectrum, 400 to 700 nm. We can also check the answer against the experimental spectrum of hydrogen in Figure 8.7. This wavelength corresponds to the turquoise line in the hydrogen spectrum.

Practice Exercises

8.4 | Calculate the wavelength in micrometers, μm, of radiation expected when $n_1 = 4$ and $n_2 = 6$. Report your result to three significant figures. (*Hint:* The values of n_1 and n_2 are used to calculate the term in parentheses first.)

8.5 | Calculate the wavelength in nanometers of the spectral line in the visible spectrum of hydrogen for which $n_1 = 2$ and $n_2 = 3$. What color is this line?

The discovery of the Rydberg equation was both exciting and perplexing. The fact that the wavelength of any line in the hydrogen spectrum can be calculated by a simple equation involving just one constant and the reciprocals of the squares of two whole numbers is remarkable. What is there about the behavior of the electron in the atom that could account for such simplicity?

8.3 | The Bohr Theory

Quantized Energies of Electrons in Atoms

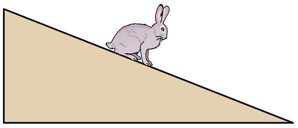
■ $E = h\nu$

$h = 6.626 \times 10^{-34}$ J s

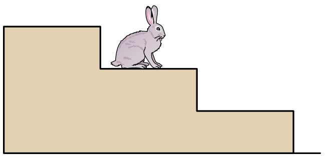
$E = (6.626 \times 10^{-34}\ \text{J s}) \times (4.567 \times 10^{14}\ \text{s}^{-1}) = 3.026 \times 10^{-19}\ \text{J}$

Earlier you saw that there is a simple relationship between the frequency of light and its energy, $E = h\nu$. Because excited atoms emit light of only certain frequencies, it must be true that only specific energy changes are able to take place within the atoms. For instance, in the spectrum of hydrogen there is a red line (see Figure 8.7) that has a wavelength of 656.4 nm and a frequency of 4.567×10^{14} Hz. As shown in the margin, the energy of a photon of this light is 3.026×10^{-19} J. Whenever a hydrogen atom emits red light, the frequency of the light is always precisely 4.567×10^{14} Hz and the energy of the atom decreases by *exactly* 3.026×10^{-19} J, never more and never less. Atomic spectra, then, tell us that *when an excited atom loses energy, not just any arbitrary amount can be lost*. The same is true if the atom gains energy.

Figure 8.8 | **An analogy of quantized states.** (*a*) The rabbit is free to move to any height less than the height of the hill. Its potential energy can take on any value between the maximum (at the hill top) and the minimum (at the bottom). Similarly, the energy of a free electron can take on any value. (*b*) The rabbit trapped inside a zoo exhibit is found only at one of the three heights: at the bottom (the lowest, or *ground state*), middle, or top step. Similarly, the energy of the electron trapped inside an atom is restricted to certain values, which correspond to the various energy levels in an atom. Some of the energy levels may be unoccupied.



(*a*) Any potential energy allowed: energy values are *continuous*



(*b*) Potential energy restricted: energy values are *discrete*

How is it that atoms of a given element always undergo exactly the same specific energy changes? The answer seems to be that in an atom an electron can have only certain definite amounts of energy and no others. We say that the electron is restricted to certain **energy levels**, and that the energy of the electron is **quantized.**

The energy of an electron in an atom might be compared to the energy of the rabbit in the exhibit shown in Figure 8.8*b*. The rabbit trapped inside this zoo exhibit can be "stable" on only one of the ledges, so it has certain specific amounts of potential energy as determined by the "energy levels" of the various ledges. If the rabbit jumps to a higher ledge, its potential energy is increased. When it hops to a lower ledge, its potential energy decreases. If the rabbit tries to occupy heights between the ledges, it immediately falls to the lower ledge. Therefore, the energy changes for the rabbit are restricted to the differences in potential energy between the ledges.

■ In a certain sense we can consider that the potential energy of the rabbit at rest is quantized.

So it is with an electron in an atom. The electron can only have energies corresponding to the set of electron energy levels in the atom. When the atom is supplied with energy (by an electric discharge, for example), an electron is raised from a low-energy level to a higher one. When the electron drops back, energy equal to the difference between the two levels is released and emitted as a photon. Because only certain energy jumps can occur, only certain frequencies of light can appear in the spectrum.

The existence of specific energy levels in atoms, as implied by atomic spectra, forms the foundation of all theories about electronic structure. Any model of the atom that attempts to describe the positions or motions of electrons must also account for atomic spectra.

The Bohr Model of Hydrogen

The first theoretical model of the hydrogen atom that successfully accounted for the Rydberg equation was proposed in 1913 by Niels Bohr (1885–1962), a Danish physicist. In his model, Bohr likened the electron moving around the nucleus to a planet circling the sun. He suggested that the electron moves around the nucleus along fixed paths, or orbits. This model broke with the classical laws of physics by placing restrictions on the sizes of the orbits and the energies that electrons could have in given orbits. This ultimately led Bohr to propose an equation that described the energy of the electron in the atom. The equation includes a number of physical constants such as the mass of the electron, its charge, and Planck's constant. It also contains an integer, n, that Bohr called a **quantum number**. Each of the orbits is identified by its value of n. When all the constants are combined, Bohr's equation becomes

$$E = \frac{-b}{n^2} \tag{8.3}$$

where E is the energy of the electron and b is the combined constant (its value is 2.18×10^{-18} J). The allowed values of n are whole numbers that range from 1 to ∞ (i.e., n could equal 1, 2, 3, 4, . . . , ∞). From this equation the energy of the electron in any particular orbit could be calculated.

■ Niels Bohr won the 1922 Nobel Prize in physics for his work on his model of the hydrogen atom.

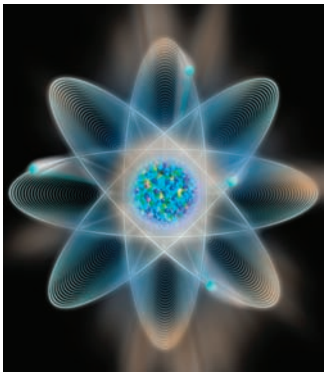
■ Classical physical laws, such as those discovered by Isaac Newton, place no restrictions on the sizes or energies of orbits.

■ Bohr's equation for the energy actually is $E = -\frac{2\pi^2 me^4}{n^2h^2}$, where m is the mass of the electron, e is the charge on the electron, n is the quantum number, and h is Planck's constant. Therefore, in Equation 8.3, $b = \frac{2\pi^2 me^4}{h^2} = 2.18 \times 10^{-18}\ \text{J}$.

Because of the negative sign in Equation 8.3, the lowest (most negative) energy value occurs when $n = 1$, which corresponds to the *first Bohr orbit*. The lowest energy state of an atom is the most stable one and is called the **ground state**. For hydrogen, the ground state occurs when its electron has $n = 1$. According to Bohr's theory, this orbit brings the electron closest to the nucleus. Conversely, an atom with $n = \infty$ would correspond to an "unbound" electron that had escaped from the nucleus. Such an electron has an energy of zero in Bohr's theory. The negative sign in Equation 8.3 ensures that any electron with a finite value of n has a lower energy than an unbound electron. Thus, energy is released when a free electron is bound to a proton to form a hydrogen atom.

When a hydrogen atom absorbs energy, as it does when an electric discharge passes through it, the electron is raised from the orbit having $n = 1$ to a higher orbit: $n = 2$ or $n = 3$ or even higher. The hydrogen atom is now in an excited state. These higher orbits are less stable than the lower ones, so the electron quickly drops to a lower orbit. When this happens, energy is emitted in the form of light (see Figure 8.9). Since the energy of the electron in a given orbit is fixed, a drop from one particular orbit to another, say, from $n = 2$ to $n = 1$, always releases the same amount of energy, and the frequency of the light emitted because of this change is always precisely the same.

The success of Bohr's theory was in its ability to account for the Rydberg equation. When the atom emits a photon, an electron drops from a higher initial energy E_{high} to a lower final energy E_{low}. If the initial quantum number of the electron is n_{high} and the final



The solar system model of the atom was the way that Niels Bohr's model was presented to the public. Today this simple picture of the atom makes a nice corporate logo, but the idea of an atom with electrons orbiting a nucleus as planets orbit a sun has been replaced by the wave mechanical model.

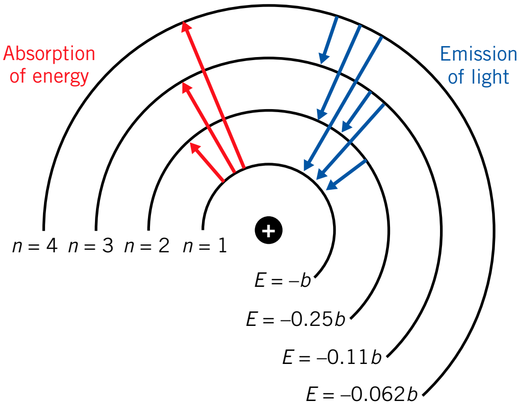


Figure 8.9 | **Absorption of energy and emission of light by the hydrogen atom.** When the atom absorbs energy, the electron is raised to a higher energy level. When the electron falls to a lower energy level, light of a particular energy and frequency is emitted.

quantum number is n_{low}, then the energy change, calculated as a positive quantity, is

$$\Delta E = E_{\text{high}} - E_{\text{low}}$$

$$= \left(\frac{-b}{n_{\text{high}}{}^2}\right) - \left(\frac{-b}{n_{\text{low}}{}^2}\right)$$

This can be rearranged to give

$$\Delta E = b\left(\frac{1}{n_{\text{low}}{}^2} - \frac{1}{n_{\text{high}}{}^2}\right) \qquad \text{with } n_{\text{high}} > n_{\text{low}}$$

By combining Equations 8.1 and 8.2, the relationship between the energy "ΔE" of a photon and its wavelength λ is

$$\Delta E = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right)$$

Substituting and solving for $1/\lambda$ give

$$\frac{1}{\lambda} = \frac{b}{hc}\left(\frac{1}{n_{\text{low}}{}^2} - \frac{1}{n_{\text{high}}{}^2}\right) \qquad \text{with } n_{\text{high}} > n_{\text{low}}$$

Notice how closely this equation derived from Bohr's theory matches the Rydberg equation, which was obtained solely from the experimentally measured atomic spectrum of hydrogen. Equally satisfying is that the combination of constants, b/hc, has a value of 109,730 cm^{-1}, which differs by only 0.05% from the experimentally derived value of R_H in the Rydberg equation.

Because Bohr envisioned the electron as being in orbit around the nucleus, the quantized energy changes also implied that there were fixed, or quantized, orbits. Angular momentum, a quantity from classical physics, describes circular motion, and Bohr derived equations in which the angular momentum would be multiples of the quantum number n. Using these equations Bohr was able to calculate the radius of the electron orbits in his model. The smallest orbit had a size of 53 pm (picometers). This distance is now known as the Bohr radius.

Failure of the Bohr Model

Bohr's model of the atom was both a success and a failure. By calculating the energy changes that occur between energy levels, Bohr was able to account for the Rydberg equation and, therefore, for the atomic spectrum of hydrogen. However, the theory was not able to explain quantitatively the spectra of atoms with more than one electron, and all attempts to modify the theory to make it work met with failure. Gradually, it became clear that Bohr's picture of the atom was flawed and that another theory would have to be found. Nevertheless, the concepts of quantum numbers and fixed energy levels were important steps forward.

8.4 | The Wave Mechanical Model

- All the objects that had been studied by scientists up until the time of Bohr's model of the hydrogen atom were large and massive in comparison with the electron, so no one had detected the limits of classical physics.
- De Broglie was awarded the Nobel Prize in physics in 1929.

Bohr's efforts to develop a theory of electronic structure were doomed from the very beginning because the classical laws of physics—those known in his day—simply do not apply to objects as small as the electron. Classical physics fails for atomic particles because matter is not really as our physical senses perceive it. When physicists were proposing that photons (particles) and the waves of electromagnetic radiation were the same thing, it became apparent that particles such as electrons may behave as waves. This idea was proposed in 1924 by a young French graduate student, Louis de Broglie.

In Section 8.1 you learned that light waves are characterized by their wavelengths and their frequencies. The same is true of matter waves. De Broglie suggested that the wavelength of a matter wave, λ, is given by the equation

$$\lambda = \frac{h}{mv} \tag{8.4}$$

where h is Planck's constant, m is the particle's mass, and v is its velocity. Notice that this equation allows us to connect a wave property, wavelength, with mass, which is characteristic of a particle. We may describe the electron either as a particle or a wave, and the de Broglie relationship provides a link between the two descriptions.

When first encountered, the concept of a particle of matter behaving as a wave rather than as a solid object is difficult to comprehend. This book certainly seems solid enough, especially if you drop it on your toe! The reason for the book's apparent solidity is that in de Broglie's equation (Equation 8.4) the mass appears in the denominator. This means that heavy objects have extremely short wavelengths. The peaks of the matter waves for heavy objects are so close together that the wave properties go unnoticed and can't even be measured experimentally. But tiny particles with very small masses have much longer wavelengths, so their wave properties become an important part of their overall behavior.

Models of the Atom

Model	Approx. Date
Indivisible particle	ca 400 BC
Billiard ball elements	1803
Plum pudding model	1897
Nuclear model	1910
Solar system model	1913
Wave mechanical model	1926

Electron Diffraction and Wave Properties of Electrons

Perhaps by now you've begun to wonder whether there is any way to *prove* that matter has wave properties. Actually, these properties can be demonstrated by a phenomenon that you have probably witnessed. When raindrops fall on a quiet pond, ripples spread out from where the drops strike the water, as shown in Figure 8.10. When two sets of ripples cross, there are places where the waves are *in phase*, which means that the peak of one wave coincides with the peak of the other. At these points the amplitudes of the waves add and the height of the water is equal to the sum of the heights of the two crossing waves. At other places the crossing waves are *out of phase*, which means the peak of one wave occurs at the trough of the other. In these places the amplitudes of the waves cancel. This reinforcement and cancellation of wave amplitudes, referred to, respectively, as *constructive* and *destructive interference*, is a phenomenon called **diffraction**. It is examined more closely in Figure 8.11. Note how diffraction creates characteristic **interference fringes** when waves pass through adjacent pinholes or reflect off closely spaced grooves. You have seen interference fringes yourself if you've ever noticed the rainbow of colors that shine from the surface of a compact disk (Figure 8.12). When white light, which contains all the visible wavelengths, is reflected from the closely spaced "bumps" on the CD, it is divided into

■ Gigantic waves, called rogue waves, with heights up to 100 ft have been observed in the ocean and are believed to be formed when a number of wave sets moving across the sea become in phase simultaneously.

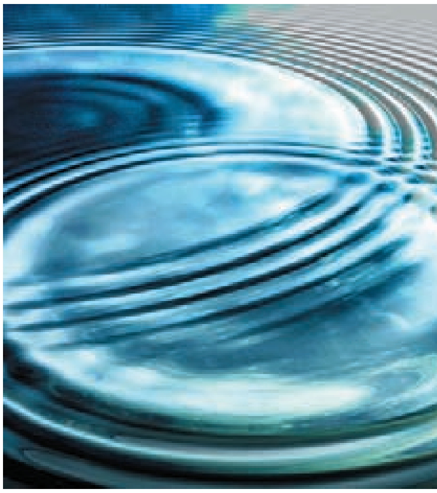


Figure 8.10 | **Diffraction of water waves on the surface of a pond.** As the waves cross, the amplitudes increase where the waves are in phase and cancel where they are out of phase. *(Mandy Collins/Alamy Images.)*

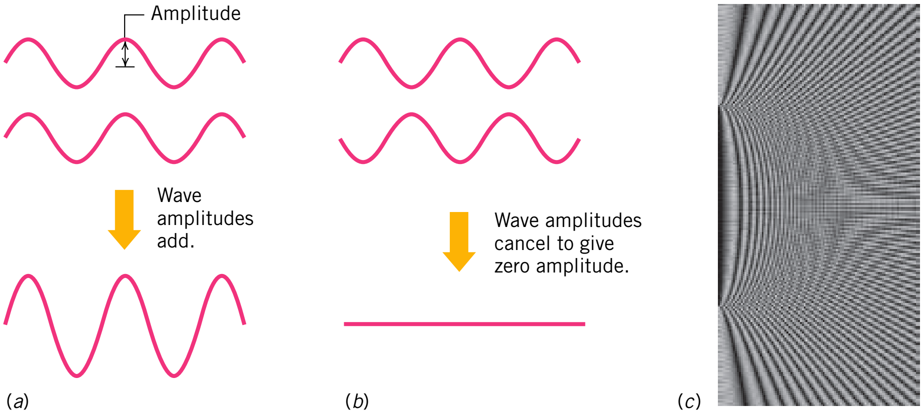


Figure 8.11 | **Constructive and destructive interference.** (*a*) Waves in phase produce constructive interference and an increase in intensity. (*b*) Waves out of phase produce destructive interference that results in the cancellation of intensity. (*c*) Waves passing through two pinholes fan out and interfere with each other, producing an interference pattern characteristic of waves. *(Zhen Lin/Wikipedia)*

Figure 8.12 | **Diffraction of light from a compact disc.** Colored interference fringes are produced by the diffraction of reflected light from the closely spaced spiral of "bumps" on the inner aluminum surface of a compact disc. *(Carol & Mike Werner/Visuals Unlimited)*

many individual light beams. For a given angle between the incoming and reflected light, the light waves experience interference with each other for all wavelengths (colors) except for one wavelength, which is reinforced. Our eye sees the wavelength of light that is reinforced, and as the angle changes the wavelengths that are reinforced change. The result is a rainbow of colors reflected from the CD.

Diffraction is a phenomenon that can be explained only as a property of waves, and we have seen how it can be demonstrated with water waves and light waves. Experiments can also be done to show that electrons, protons, and neutrons experience diffraction, which demonstrates their wave nature (see Figure 8.13). In fact, electron diffraction is the principle on which the electron microscope is based (See *Chemistry and Current Affairs 8.1*).

CHEMISTRY AND CURRENT AFFAIRS | 8.1

The Electron Microscope

The usefulness of a microscope in studying small specimens is limited by its ability to distinguish between closely spaced objects. We call this ability the *resolving power* of the microscope. Through optics, it is possible to increase the magnification and thereby increase the resolving power, but only within limits. These limits depend on the wavelength of the light that is used. Objects with diameters less than the wavelength of the light cannot be seen in detail. Since the smallest wavelength of visible light is about 400 nm, objects smaller than this can't be seen clearly with a microscope that uses visible light.

The electron microscope uses electron waves to "see" very small objects. De Broglie's equation, $\lambda = h/mv$, suggests that if an electron, proton, or neutron has a very high velocity, its wavelength will be very small. In the electron microscope, high-voltage electrodes accelerate electrons. This gives electron waves with typical wavelengths of about 2 pm to 12 pm that strike the sample and are then focused magnetically (using "magnetic lenses") onto a fluorescent screen where they form a visible image. Because of certain difficulties, the actual resolving power of the instrument is quite a bit less than the wavelength of the electron waves—generally on the order of 1 to 6 nm. Some high-resolution electron microscopes, however, are able to reveal the shadows of individual atoms in very thin specimens through which the electron beam passes.

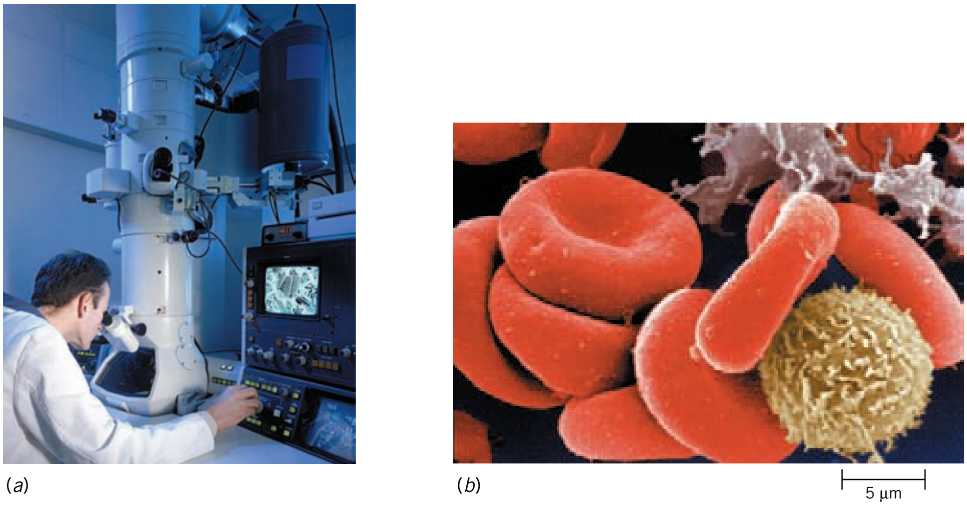


Figure 1 A modern electron microscope (*a*) operated by a trained technician is used to obtain (*b*) electron micrographs such as the one shown here depicting red and white blood cells. *(Brand X/Superstock; Yorgos Nikas/Stone/Getty Images)*

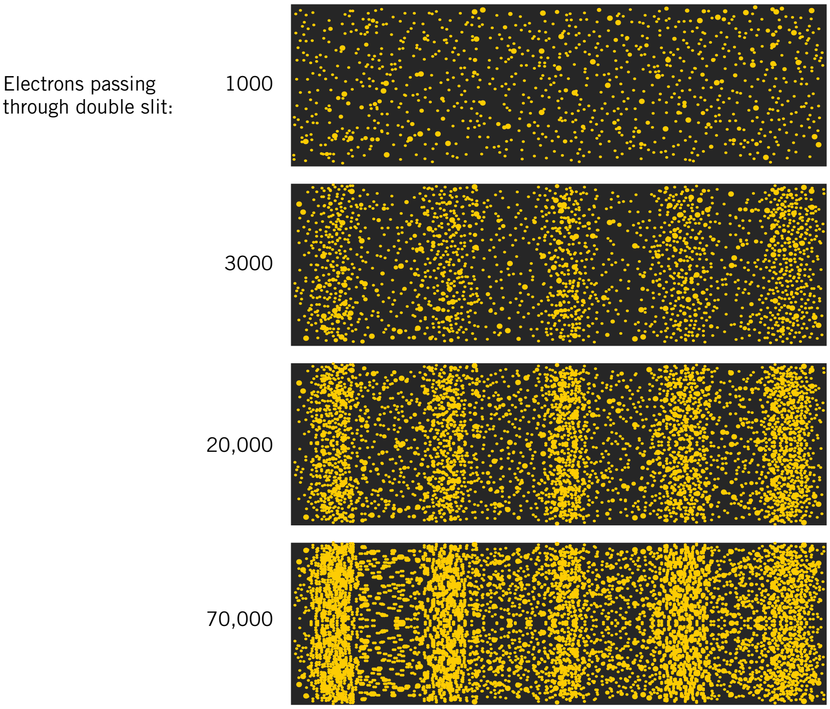


Figure 8.13 | **Experimental evidence of wave behavior in electrons.** (*a*) Electrons passing one at a time through a double slit. Each spot shows an electron impact on a detector. As more and more electrons are passed through the slits, interference fringes are observed. *(Semiconductor Surface Physics Group, Queen's University.)*

Quantized Energy of Bound Electrons

Standing Waves and Quantum Numbers

Before we can discuss how electron waves behave in atoms, we need to know a little more about waves in general. There are basically two kinds of waves, *traveling waves* and *standing waves*. On a lake or ocean the wind produces waves whose crests and troughs move across the water's surface, as shown in Figure 8.14. The water moves up and down while the crests and troughs travel horizontally in the direction of the wind. These are examples of **traveling waves.**

A more important kind of wave for us is the standing wave. An example is the vibrating string of a guitar. When the string is plucked, its center vibrates up and down while the ends, of course, remain fixed. The crest, or point of maximum amplitude of the wave, occurs at one position. At the ends of the string are points of zero amplitude, called **nodes**, and their positions are also fixed. A **standing wave**, then, is one in which the crests and nodes

■ The wavelength of this wave is actually twice the length of the string.

Figure 8.14 | **Traveling waves.** Waves breaking on this beach are the result of traveling waves from out in the ocean. *(Gallo Images/ Alamy)*

do not change position. One of the interesting things about standing waves is that they lead naturally to "quantum numbers." Let's see how this works using the guitar as an example.

As you know, many notes can be played on a guitar string by shortening its effective length with a finger placed at frets along the neck of the instrument. But even without shortening the string, we can play a variety of notes. For instance, if the string is touched momentarily at its midpoint at the same time it is plucked, the string vibrates as shown in Figure 8.15 and produces a tone an octave higher. The wave that produces this higher tone has a wavelength exactly half of that formed when the untouched string is plucked. In Figure 8.15 we see that other wavelengths are possible, too, and each gives a different note.

■ Notes played this way are called harmonics.

If you examine Figure 8.15, you will see that there are some restrictions on the wavelengths that can exist. Not just any wavelength is possible, because the nodes at either end of the string are in fixed positions. The only waves that can occur are those for which a half-wavelength is repeated *exactly* a whole number of times. Expressed another way, the length of the string is a whole-number multiple of half-wavelengths. In a mathematical form we could write this as

$$L = n\left(\frac{\lambda}{2}\right)$$

where L is the length of the string, λ is a wavelength (therefore, $\lambda/2$ is half the wavelength), and n is an integer. Rearranging this to solve for the wavelength gives

$$\lambda = \frac{2L}{n} \tag{8.5}$$

Notes played on a guitar rely on standing waves. The ends of the strings correspond to nodes of the standing waves. Different notes can be played by shortening the effective lengths of the strings with fingers placed along the neck of the instrument. *(SuperStock/Age Fotostock America, Inc.)*

We see that the waves that are possible are determined quite naturally by a set of whole numbers (similar to quantum numbers).

We are now in a position to demonstrate how quantum theory unites wave and particle descriptions to build a simple but accurate model of a bound electron. Let's look at an electron that is confined to a wire of length L. To keep things simple, let's assume that the wire is infinitely thin, so that the electron can only move in straight lines along the wire. The wire is clamped in place at either end, and its ends cannot move up or down.

First, let's consider a classical particle model: the "bead on a wire" model shown in Figure 8.16*a*. The bead can slide in either direction along the wire, like a bead on an abacus. If the bead's mass is m and its velocity is v, its kinetic energy is given by

$$E = \frac{1}{2}mv^2$$

The bead can have any velocity, even zero, so the energy E can have any value, even zero. No position on the wire is any more favorable than any other, and the bead is equally likely to be found anywhere on the wire. There is no reason why the bead's position and velocity cannot be known simultaneously.

Now consider a classical wave along the wire, Figure 8.16*b*. It is exactly like the guitar string we looked at in Figure 8.15. The ends of the wire are clamped in place, so there *must* be a whole number of peaks and troughs along the wire. The wavelength is restricted to values calculated by Equation 8.5. We can see that the quantum number, n, is just the

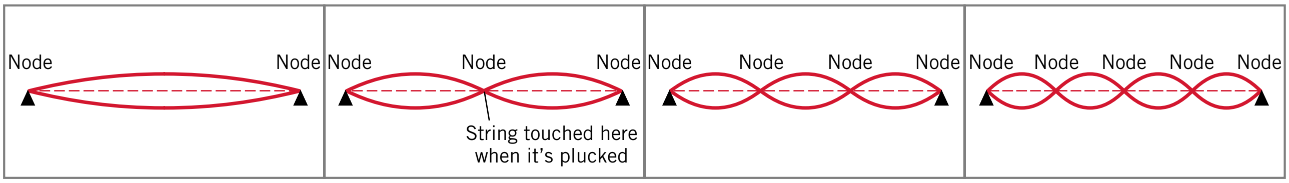


Figure 8.15 | **Standing waves on a guitar string.** Panes show 1, 2, 3, and 4 half-waves, respectively. The number of nodes is one more than the number of half-waves.

number of peaks and troughs along the wave. It has integer values (1, 2, 3, . . .) because you can't have half a peak or half a trough.

Now let's use the de Broglie relation, Equation 8.4, to unite these two classical models. Our goal is to derive an expression for the energy of an electron trapped on the wire (Figure 8.16*c*). The de Broglie relation lets us relate particle velocities with wavelengths. Rearranging Equation 8.4, we have

$$v = \left(\frac{h}{m\lambda}\right)$$

and inserting this equation for kinetic energy gives

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2$$
$$= \frac{h^2}{2m\lambda^2}$$

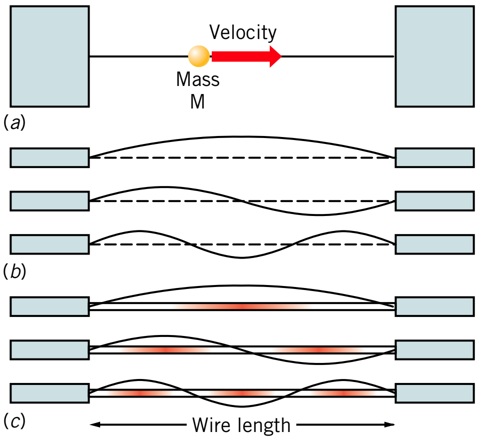


Figure 8.16 | **Three models of an electron on an infinitely thin wire of length *L*.** (*a*) Classical model. Bead can have any velocity or position. (*b*) Classical waves like a guitar string. (*c*) Quantum mechanical model where wave amplitude is related to the probability of the bead's position.

This equation will give us the energy of the electron from its wavelength. We can replace λ with its equivalent values shown Equation 8.5, which gives the wavelength of the standing wave in terms of the wire length L and the quantum number n. The result is

$$E = \frac{n^2h^2}{8mL^2} \tag{8.6}$$

This equation has a number of profound implications. The fact that the electron's energy depends on an integer, n, means that *only certain energy states are allowed.* The allowed states are plotted on the energy level diagram shown in Figure 8.17. The lowest value of n is 1, so the lowest energy level (the ground state) is $E = h^2/8mL^2$. Energies lower than this are not allowed, so the energy cannot be zero! This indicates that the electron will always have some residual kinetic energy. The electron is never at rest. This is true for the electron trapped in a wire and it is also true for an electron trapped in an atom. Thus, *quantum theory resolves the collapsing atom paradox.*

Note that the spacing between energy levels is proportional to $1/L^2$. This means that when the wire is made longer, the energy levels become more closely spaced. In general, *the more room an electron has to move in, the smaller the spacings between its energy levels.* Chemical reactions sometimes change the way that electrons are confined in molecules. This causes changes in the wavelengths of light the reacting mixture absorbs. These wavelength changes are why color changes sometimes occur during chemical reactions.

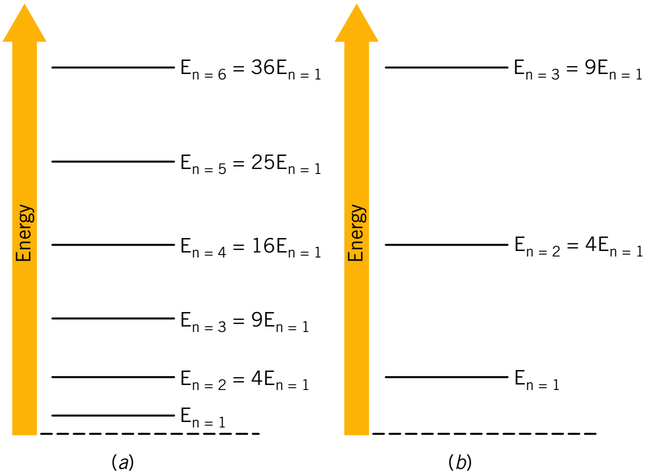


Figure 8.17 | **Energy level diagram for the electron-on-a-wire model.** (*a*) A long wire, with $L = 2$ nm, and (*b*) a short wire, with $L = 1$ nm. The value of n at each energy level indicates the number of peaks and troughs of the wave. Notice how the energy levels become more closely spaced when the electron has more room to move. Notice also that the energy in the ground state ($E_{n=1}$) is not zero.

Wave Functions

A **wave function** (symbolized by the symbol ψ, the Greek letter psi) is the quantum mechanical description of an electron. This mathematical construct, based on the quantum numbers, can be used to describe the shape of the electron wave and its energy. The wave function is not an oscillation of the wire, like a guitar wave, nor is it an electromagnetic wave. The wave's amplitude at any given point can be related to the probability of finding the electron there.

The electron waves shown in Figure 8.16*c* show that unlike the bead-on-a-wire model, the electron is more likely to be found at some places on the wire than others. For the ground state, with $n = 1$, the electron is most likely to be found in the center of the wire. Where the

■ The probability of finding an electron at a given point is proportional to the amplitude of the electron wave squared. Thus, peaks and troughs in the electron wave indicate places where there is the greatest buildup of negative charge.

amplitude is zero, such as at the ends of the wire or the center of the wire in the $n = 2$ state, there is a zero probability of finding the electron! Points where the amplitude of the electron wave is zero are called **nodes**. Notice that the higher the quantum number n, the more nodes the electron wave has, and from Equation 8.6, the more energy the electron has. It is generally true that *the more nodes an electron wave has, the higher its energy.*

8.5 | Quantum Numbers of Electrons in Atoms

In 1926 Erwin Schrödinger (1887–1961), an Austrian physicist, became the first scientist to successfully apply the concept of the wave nature of matter to an explanation of electronic structure. His work and the theory that developed from it are highly mathematical. Fortunately, we need only a qualitative understanding of electronic structure, and the main points of the theory can be understood without all the math.

■ Schrödinger won the Nobel Prize in physics in 1933 for his work. The equation he developed that gives electronic wave functions and energies is known as *Schrödinger's equation*. The equation is extremely difficult to solve. Even an approximate solution of the equation for large molecules can require hours or days of supercomputer time.

Electron Waves in Atoms Are Called Orbitals

Schrödinger developed an equation that can be solved to give wave functions and energy levels for electrons trapped inside atoms. Wave functions for electrons in atoms are called **orbitals.** Not all of the energies of the waves are different, but most are. *Energy changes within an atom are simply the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy.*

■ Electron waves are described by the term *orbital* to differentiate them from the notion of *orbits,* which was part of the Bohr model of the atom.

We will be interested in two properties of orbitals, their energies and their shapes. Their energies are important because when an atom is in its most stable state (its *ground state*), the atom's electrons have waveforms with the lowest possible energies. The shapes of the wave patterns (i.e., where their amplitudes are large and where they are small) are important because the theory tells us that the amplitude of a wave at any particular place is related to the likelihood of finding the electron there. This will be important when we study how and why atoms form chemical bonds to each other.

■ "Most stable" almost always means "lowest energy."

In much the same way that the characteristics of a wave on a one-dimensional guitar string can be related to a single integer, wave mechanics tells us that the three-dimensional electron waves (orbitals) can be characterized by a set of *three* integer quantum numbers, n, ℓ, and m_ℓ. In discussing the energies of the orbitals, it is usually most convenient to sort the orbitals into groups according to these quantum numbers.

The Principal Quantum Number, *n*

The quantum number n is called the **principal quantum number**, and all orbitals that have the same value of n are said to be in the same **shell**. The values of n can range from $n = 1$ to $n = \infty$. The shell with $n = 1$ is called the *first shell,* the shell with $n = 2$ is the *second shell,* and so forth. The various shells are also sometimes identified by letters, beginning (for no significant reason) with K for the first shell ($n = 1$).

■ The term shell comes from an early notion that electrons are arranged in atoms in a manner similar to the layers, or shells, found within an onion.

The principal quantum number is related to the size of the electron wave (i.e., how far the wave effectively extends from the nucleus). The higher the value of n, the larger is the electron's average distance from the nucleus. This quantum number is also related to the energy of the orbital. As n increases, the energies of the orbitals also increase.

Bohr's theory took into account only the principal quantum number n. His theory worked fine for hydrogen because hydrogen just happens to be the one element in which all orbitals having the same value of n also have the same energy. Bohr's theory failed for atoms other than hydrogen, however, because when the atom has more than one electron, orbitals with the same value of n can have different energies.

■ Bohr was fortunate to have used the element hydrogen to develop his model of the atoms. If he had chosen a different element, his model would never have worked.

The Secondary Quantum Number, ℓ

The **secondary quantum number, ℓ**, divides the shells into smaller groups of orbitals called **subshells**. The value of n determines which values of ℓ are allowed. For a given n, ℓ can

■ ℓ is also called the **azimuthal quantum number** and the **orbital angular momentum number**.

range from $\ell = 0$ to $\ell = (n - 1)$. Thus, when $n = 1$, $(n - 1) = 0$, so the only value of ℓ that's allowed is zero. This means that when $n = 1$, there is only one subshell (the shell and subshell are really identical). When $n = 2$, ℓ can have a value of 0 or 1. (The maximum value of $\ell = n - 1 = 2 - 1 = 1$.) This means that when $n = 2$, there are two subshells. One has $n = 2$ and $\ell = 0$, and the other has $n = 2$ and $\ell = 1$. The relationship between n and the allowed values of ℓ are summarized in the table in the margin.

Relationship between n and ℓ

Value of n	Value of ℓ
1	0
2	0, 1
3	0, 1, 2
4	0, 1, 2, 3
5	0, 1, 2, 3, 4
n	0, 1, 2, … $(n - 1)$

Subshells could be identified by the numerical value of ℓ. However, to avoid confusing numerical values of n with those of ℓ, a letter code is normally used to specify the value of ℓ.

Value of ℓ	0	1	2	3	4	5	. . .
Letter designation	*s*	*p*	*d*	*f*	*g*	*h*	. . .

To designate a particular subshell, we write the value of its principal quantum number followed by the letter code for the subshell. For example, the subshell with $n = 2$ and $\ell = 1$ is the 2*p* subshell; the subshell with $n = 4$ and $\ell = 0$ is the 4*s* subshell. Notice that because of the relationship between n and ℓ, every shell has an *s* subshell (1*s*, 2*s*, 3*s*, etc.). All the shells except the first have a *p* subshell (2*p*, 3*p*, 4*p*, etc.). All but the first and second shells have a *d* subshell (3*d*, 4*d*, etc.); and so forth.

■ The number of subshells in a given shell equals the value of n for that shell. For example, when $n = 3$, there are three subshells.

Practice Exercises

8.6 | What are the values of n and ℓ for the following subshells? (a) 4*d*, (b) 5*f*, and (c) 7*s* (*Hint:* How are the subshell designations related to the value of ℓ?)

8.7 | What subshells would be found in the shells with $n = 2$ and $n = 5$? How is the number of subshells related to n?

The secondary quantum number determines the shape of the orbital, which we will examine more closely later. Except for the special case of hydrogen, which has only one electron, the value of ℓ also indicates the relative energies of the orbitals. This means that in atoms with two or more electrons, the subshells within a given shell differ slightly in energy, with the energy of the subshell increasing with increasing ℓ. Therefore, within a given shell, the *s* subshell is lowest in energy, *p* is the next lowest, followed by *d*, then *f*, and so on. For example,

$$4s < 4p < 4d < 4f$$

$$\text{— increasing energy} \rightarrow$$

The Magnetic Quantum Number, m_ℓ

The third quantum number, m_ℓ, is known as the **magnetic quantum number**. It divides the subshells into individual orbitals, and its values are related to the way the individual orbitals are oriented relative to each other in space. As with ℓ, there are restrictions as to the possible values of m_ℓ, which can range from $+\ell$ to $-\ell$. When $\ell = 0$, m_ℓ can have only the value 0 because +0 and −0 are the same. An *s* subshell, then, has just a single orbital. When $\ell = 1$, the possible values of m_ℓ are +1, 0, and −1. A *p* subshell therefore has three orbitals: one with $\ell = 1$ and $m_\ell = 1$, another with $\ell = 1$ and $m_\ell = 0$, and a third with $\ell = 1$ and $m_\ell = -1$. Similarly, we find that a *d* subshell has five orbitals and an *f* subshell has seven orbitals. The numbers of orbitals in the subshells are easy to remember because they follow a simple arithmetic progression.

■ Spectroscopists used m_ℓ to explain additional lines that appear in atomic spectra when atoms emit light while in a magnetic field. This explains how this quantum number got its name.

s	*p*	*d*	*f*	. . .
1	3	5	7	. . .

The Whole Picture

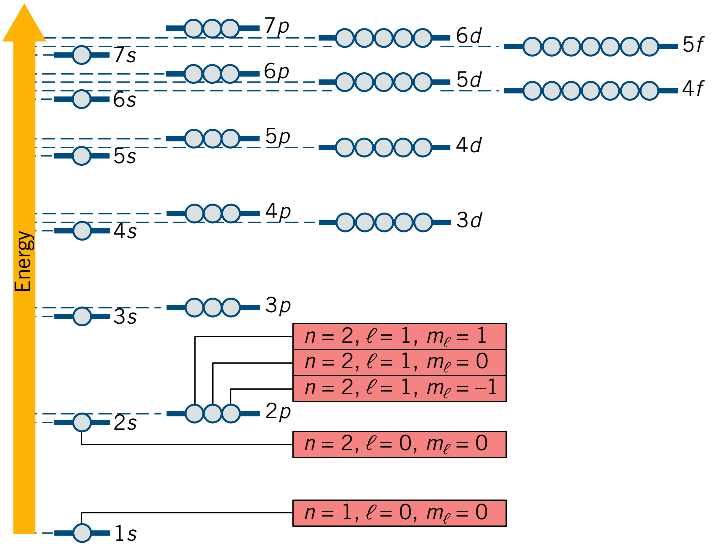
The relationships among all three quantum numbers are summarized in Table 8.1. In addition, the relative energies of the subshells in an atom containing two or more electrons are depicted in Figure 8.18. Several important features should be noted. First, observe that each orbital on this energy diagram is indicated by a separate circle—one for an *s* subshell,

Table 8.1 **Summary of Relationships among the Quantum Numbers n, ℓ, and m_ℓ**

Value of n	Value of ℓ	Value of m_ℓ	Subshell	Number of Orbitals
1	0	0	1*s*	1
2	0	0	2*s*	1
	1	−1, 0, 1	2*p*	3
3	0	0	3*s*	1
	1	−1, 0, 1	3*p*	3
	2	−2, −1, 0, 1, 2	3*d*	5
4	0	0	4*s*	1
	1	−1, 0, 1	4*p*	3
	2	−2, −1, 0, 1, 2	4*d*	5
	3	−3, −2, −1, 0, 1, 2, 3	4*f*	7

three for a *p* subshell, and so forth. Second, notice that all the orbitals of a given subshell have the *same* energy. Third, note that, in going upward on the energy scale, the spacing between successive shells decreases as the number of subshells increases. This leads to the overlapping of shells having different values of *n*. For instance, the 4*s* subshell is lower in energy than the 3*d* subshell, 5*s* is lower than 4*d*, and 6*s* is lower than 5*d*. In addition, the 4*f* subshell is below the 5*d* subshell and 5*f* is below 6*d*.

We will see shortly that Figure 8.18 is very useful for predicting the electronic structures of atoms. Before discussing this, however, we must study another very important property of the electron, a property called spin. Electron spin gives rise to a fourth quantum number.



7p
6d
5f
7s
6p
5d
4f
6s
5p
4d
5s
4p
3d
4s
Energy
3p
3s
$n = 2, \ell = 1, m_\ell = 1$
$n = 2, \ell = 1, m_\ell = 0$
$n = 2, \ell = 1, m_\ell = -1$
2p
2s
$n = 2, \ell = 0, m_\ell = 0$
$n = 1, \ell = 0, m_\ell = 0$
1s

Figure 8.18 | **Approximate energy level diagram for atoms with two or more electrons.** The quantum numbers associated with the orbitals in the first two shells are also shown.

■ In an atom, an electron can take on many different energies and wave shapes, each of which is called an orbital that is identified by a set of values for n, ℓ, and m_ℓ. When the electron wave possesses a given set of n, ℓ, and m_ℓ, we say the electron "occupies the orbital" with that set of quantum numbers.

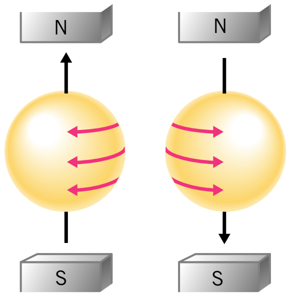
8.6 | Electron Spin

Recall from Section 8.3 that an atom is in its most stable state (its ground state) when its electrons have the lowest possible energies. This occurs when the electrons "occupy" the lowest energy orbitals that are available. But what determines how the electrons "fill" these orbitals? Fortunately, there are some simple rules that can help. These govern both the maximum number of electrons that can be in a particular orbital and how orbitals with the same energy become filled. One important factor that influences the distribution of electrons is the phenomenon known as *electron spin*.

Spin Quantum Number

When a beam of atoms with an odd number of electrons is passed through an uneven magnetic field, the beam is split in two, as shown in Figure 8.19. The splitting occurs because the electrons within the atoms interact with the magnetic field in two different ways. The electrons behave like tiny magnets, and they are attracted to one or the other of the poles depending on their orientation. This can be explained by imagining that an electron spins around its axis, like a toy top. A moving charge creates a moving electric field, which in turn creates a magnetic field. The spinning electrical charge of the electron creates its own magnetic field. This **electron spin** could occur in two possible directions, which accounts for the two beams.

Electron spin gives us a fourth quantum number for the electron, called the **spin quantum number, m_s**, which can take on two possible values: $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$, corresponding to the two beams in Figure 8.19. The actual values of m_s and the reason they are not integers aren't very important to us, but the fact that there are *only* two values is very significant.



The electron can spin in either of two directions in the presence of an external magnetic field. Without a magnetic field the electrons and their spins are usually oriented in random directions.

Pauli Exclusion Principle

In 1925 an Austrian physicist, Wolfgang Pauli (1900–1958), expressed the importance of electron spin in determining electronic structure. The **Pauli exclusion principle** states that *no two electrons in the same atom can have identical values for all four of their quantum numbers.* To understand the significance of this, suppose two electrons were to occupy the 1*s* orbital of an atom. Each electron would have $n = 1$, $\ell = 0$, and $m_\ell = 0$. Since these three quantum numbers are the same for both electrons, the exclusion principle requires that their fourth quantum numbers (their spin quantum numbers) be different; one electron must have $m_s = +\frac{1}{2}$ and the other, $m_s = -\frac{1}{2}$. No more than two electrons can occupy the 1*s* orbital of the atom simultaneously because there are only two possible values of m_s. Thus, the Pauli exclusion principle is really telling us that *the maximum number of electrons in any orbital is two*, and that *when two electrons are in the same orbital, they must have opposite spins*.

■ Electrons don't actually spin, but it is useful to picture the electron as spinning.

■ Pauli received the 1945 Nobel Prize in physics for his discovery of the exclusion principle.

The limit of two electrons per orbital also limits the maximum electron populations of the shells and subshells. For the subshells we have

Subshell	Number of Orbitals	Maximum Number of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

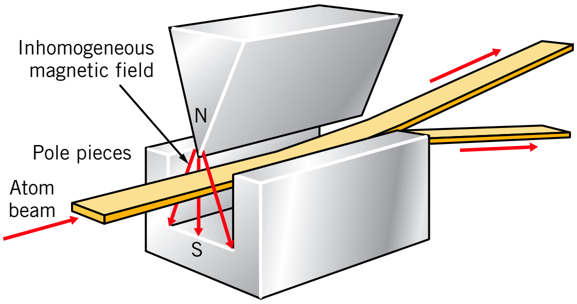


Figure 8.19 | **The discovery of electron spin.** In this classic experiment by Stern and Gerlach, a beam of atoms with an odd number of electrons is passed through an uneven magnetic field, created by magnet pole faces of different shapes. The beam splits in two, indicating that the electrons in the atoms behave as tiny magnets, which are attracted to one or the other of the poles depending on their orientation. Electron spin was proposed to account for the two possible orientations for the electron's magnetic field.

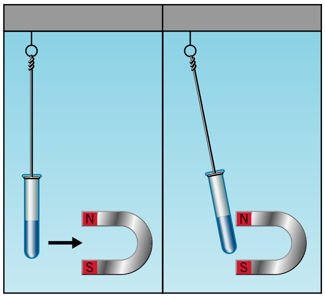
The maximum electron population per shell is shown below.

Shell	Subshells	Maximum Shell Population	
1	1*s*	2	
2	2*s* 2*p*	8	(2 + 6)
3	3*s* 3*p* 3*d*	18	(2 + 6 + 10)
4	4*s* 4*p* 4*d* 4*f*	32	(2 + 6 + 10 + 14)

Remember that a shell is a group of orbitals with the same value of *n*. A subshell is a group of orbitals with the same values of *n* and ℓ.

The maximum electron population of a shell is $2n^2$.

Paramagnetism and Diamagnetism



A paramagnetic substance is attracted to a magnetic field.

We have seen that when two electrons occupy the same orbital they must have different values of m_s. When this occurs, we say that the spins of the electrons are *paired,* or simply that the electrons are *paired.* Such pairing leads to the cancellation of the magnetic effects of the electrons because the north pole of one electron magnet is opposite the south pole of the other. Atoms with more electrons that spin in one direction than in the other are said to contain *unpaired* electrons. For these atoms, the magnetic effects do not cancel and the atoms themselves become tiny magnets that can be attracted to an external magnetic field. This weak attraction of a substance containing unpaired electrons to a magnet is called **paramagnetism**. Substances in which all the electrons are paired are not attracted to a magnet and are said to be diamagnetic.

Diamagnetic substances are actually weakly repelled by a magnetic field.

Paramagnetism and **diamagnetism** are measurable properties that provide experimental verification of the presence or absence of unpaired electrons in substances. In addition, the quantitative measurement of the strength of the attraction of a paramagnetic substance toward a magnetic field makes it possible to calculate the number of unpaired electrons in its atoms, molecules, or ions.

8.7 | Energy Levels and Ground State Electron Configurations

The distribution of electrons among the orbitals of an atom is called the atom's **electronic structure** or **electron configuration.** This is very useful information about an element because the arrangement of electrons in the outer parts of an atom, which is determined by its electron configuration, controls the chemical properties of the element.

We are interested in the ground state electron configurations of the elements. This is the configuration that yields the lowest energy for an atom and can be predicted for many of the elements by the use of the energy level diagram in Figure 8.18 and application of the Pauli exclusion principle. To see how we go about this, let's begin with the simplest atom of all, hydrogen.

Hydrogen has an atomic number, *Z*, equal to 1, so a neutral hydrogen atom has one electron. In its ground state this electron occupies the lowest energy orbital that's available, which is the 1*s* orbital. To indicate symbolically the electron configuration we list the subshells that contain electrons and indicate their electron populations by appropriate superscripts. Thus, the electron configuration of hydrogen is written as

$$\text{H} \qquad 1s^1$$

Another way of expressing electron configurations that we will sometimes find useful is the **orbital diagram**. In it, a circle will represent each orbital and arrows will be used to indicate the individual electrons, head up for spin in one direction and head down for spin in the other. The orbital diagram for hydrogen is simply

$$\text{H} \qquad \underset{1s}{\textcircled{\uparrow}}$$

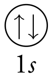
Ground State Electron Configurations

To arrive at the electron configuration of an atom of another element, we imagine that we begin with a hydrogen atom and then add one proton after another (plus whatever neutrons are also needed) until we obtain the nucleus of the atom of interest. As we proceed, we also add electrons, one at a time to the lowest available orbital, until we have added enough electrons to give the neutral atom of the element. This imaginary process for obtaining the electronic structure of an atom is known as the **aufbau principle**. The word *aufbau* is German for *building up*.

How *s* Orbitals Fill

Let's look at the way this works for helium, which has $Z = 2$. This atom has two electrons, both of which occupy the 1*s* orbital. The electron configuration of helium can therefore be written as

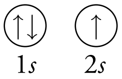
He $1s^2$ or He



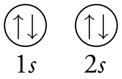
Notice that the orbital diagram shows that both electrons in the 1*s* orbital are paired.

We can proceed in the same fashion to predict successfully the electron configurations of most of the elements in the periodic table. For example, the next two elements in the table are lithium, Li ($Z = 3$), and beryllium, Be ($Z = 4$), which have three and four electrons, respectively. For each of these, the first two electrons enter the 1*s* orbital with their spins paired. The Pauli exclusion principle tells us that the 1*s* subshell is filled with two electrons, and Figure 8.18 shows that the orbital of next lowest energy is the 2*s*, which can also hold up to two electrons. Therefore, the third electron of lithium and the third and fourth electrons of beryllium enter the 2*s*. We can represent the electronic structures of lithium and beryllium as

Li $1s^22s^1$ or Li



Be $1s^22s^2$ or Be



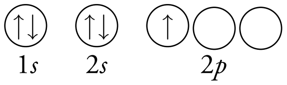
Filling *p* and *d* Orbitals

After beryllium comes boron, B ($Z = 5$). Referring to Figure 8.18, we see that the first four electrons of this atom complete the 1*s* and 2*s* subshells, so the fifth electron must be placed into the 2*p* subshell.

B $1s^22s^22p^1$

In the orbital diagram for boron, the fifth electron can be put into any one of the 2*p* orbitals—which one doesn't matter because they are all of equal energy.

B

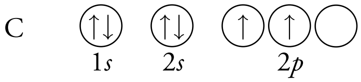


Notice, however, that when we give this orbital diagram we show *all* of the orbitals of the 2*p* subshell even though two of them are empty.

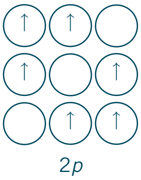
Next we come to carbon, which has six electrons. As before, the first four electrons complete the 1*s* and 2*s* orbitals. The remaining two electrons go in the 2*p* subshell to give

C $1s^22s^22p^2$

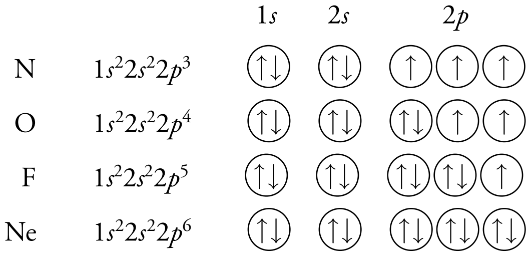
Now, however, to write the orbital diagram we have to make a decision as to where to put the two *p* electrons. (At this point you may have an unprintable suggestion! But try to bear up. It's really not all that bad.) To make this decision, we apply **Hund's rule**, which states that *when electrons are placed in a set of orbitals of equal energy, they are spread out as much as* *possible to give as few paired electrons as possible.* Both theory and experiment have shown that if we follow this rule, we obtain the electron configuration with the lowest energy. For carbon, it means that the two *p* electrons are in separate orbitals and their spins are in the same direction.[1]



■ It doesn't matter which two orbitals are shown as occupied. Any of these are okay for the ground state of carbon.



Applying the Pauli exclusion principle and Hund's rule, we can now complete the electron configurations and orbital diagrams for the rest of the elements of the second period.



We can continue to predict electron configurations in this way, using Figure 8.18 as a guide to tell us which subshells become occupied and in what order. For instance, after completing the 2*p* subshell at neon, Figure 8.18 predicts that the next two electrons enter the 3*s*, followed by the filling of the 3*p*. Then we find the 4*s* lower in energy than the 3*d*, so it is filled first. Next, the 3*d* is completed before we go on to fill the 4*p*, and so forth.

You might be thinking that you'll have to consult Figure 8.18 whenever you need to write down the ground state electron configuration of an element. However, as you will see in the next section, all the information contained in this figure is also contained in the periodic table.

8.8 | Periodic Table and Ground State Electron Configurations

In Chapter 3 you learned that when Mendeleev constructed his periodic table, elements with similar chemical properties were arranged in vertical columns called groups. Later work led to the expanded version of the periodic table we use today. The basic structure of this table is one of the strongest empirical supports for the quantum theory, and it also permits us to use the periodic table as a device for predicting electron configurations.

Predicting Ground State Electron Configurations

Consider, for example, the way the table is laid out (Figure 8.20). On the left there is a block of *two* columns shown in blue; on the right there is a block of *six* columns shown in pink; in the center there is a block of *ten* columns shown in yellow, and below the table

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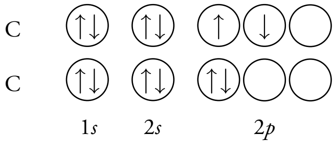
[1] Hund's rule gives us the *lowest* energy (ground state) distribution of electrons among the orbitals. However, configurations such as



are not impossible—it is just that neither of them corresponds to the lowest energy distribution of electrons in the carbon atom.

there are two rows consisting of *fourteen* elements each shown in gray. These numbers—2, 6, 10, and 14—are *precisely* the numbers of electrons that the quantum theory tells us can occupy *s*, *p*, *d*, and *f* subshells, respectively. In fact, *we can use the structure of the periodic table to predict the filling order of the subshells when we write the electron configuration of an element.*

■ This would be an amazing coincidence if the theory were wrong!

TOOLS

Periodic table and electron configurations

To use the periodic table to predict electron configurations, we follow the aufbau principle as before. We start with hydrogen and then move through the table row after row until we reach the element of interest, noting as we go along which regions of the table we pass through. For example, consider the element calcium. Using Figure 8.21, we obtain the electron configuration

$$\text{Ca} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

Refer to a periodic table and Figure 8.21 as we go through the process of writing an electron configuration.

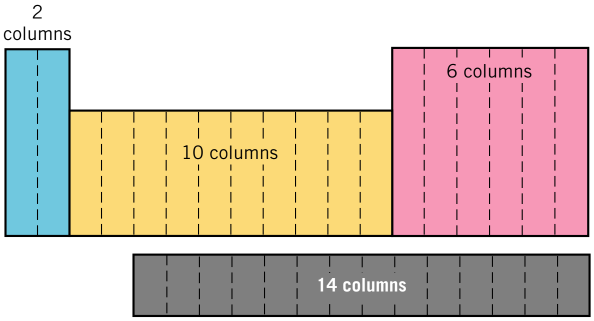


Figure 8.20 | **The overall column structure of the periodic table.** The table is naturally divided into regions of 2, 6, 10, and 14 columns, which are the numbers of electrons that can occupy *s*, *p*, *d*, and *f* subshells.

Filling Periods 1, 2, and 3

Notice that the first period has only two elements, H and He. Starting with hydrogen and passing through this period, two electrons are added to the atom. These enter the 1*s* subshell and are written as $1s^2$. Next we move across the second period, where the first two elements, Li and Be, are in the block of two columns. The two electrons added here enter the 2*s* subshell and are written as $2s^2$. Then we move to the block of six columns, and as we move across this region in the second row we fill the 2*p* subshell with six electrons, writing $2p^6$. Now we go to the third period, where we first pass through the block of two columns, filling the 3*s* subshell with two electrons, $3s^2$, and then through the block of six columns, filling the 3*p* subshell with six electrons, $3p^6$.

Filling Periods 4 and 5

Next, we move to the fourth period. To get to calcium in the example above we step through two elements in the two-column block, filling the 4*s* subshell with two electrons. Up to calcium we have only filled *s* and *p* subshells. Figure 8.21 shows that after calcium the 3*d* subshell is the next to be filled. Ten electrons are added for the ten elements in the first row of the transition elements. After the 3*d* subshell we complete the fourth period by filling the 4*p* subshell with six electrons. The fifth period fills the 5*s*, 4*d*, and 5*p* subshells in sequence with 2, 10, and 6 electrons, respectively.

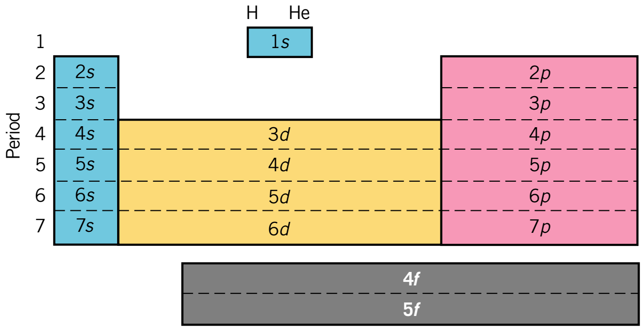


Figure 8.21 | **Arrangement of subshells in the periodic table.** This format illustrates the sequence for filling subshells.

Filling Periods 6 and 7

The inner transition elements (*f* subshells) begin to fill in the 6th and 7th periods. Period six fills the 6*s*, 4*f*, 5*d*, and 6*p* subshells with 2, 14, 10, and 6 electrons, respectively. There are many irregularities in this sequence, and Appendix C.1 should be consulted for the correct electron configurations. The seventh period fills the 7*s*, 5*f*, 6*d*, and 7*p* subshells. Once again, the sequence is based on the energies of the subshells, and there are many irregularities that make it advisable to consult Appendix C.1 for the correct electron configurations.

Notice that in the above patterns the *s* and *p* subshells always have the same number as the period they are in. The *d* subshells always have a number that is one less than the period they are in. Finally, the *f* subshells are always two less than the period in which they reside.

Example 8.4

Predicting Electron Configurations

What is the electron configuration of (a) Mn and (b) Bi?

■ **Analysis:** We need to write the correct sequence of subshells along with the correct number of electrons, written as superscripts, in each subshell until we have the correct number of electrons for (a) Mn and (b) Bi.

■ **Assembling the Tools:** We use the periodic table as a tool to tell us which subshells become filled. It is best to do this without referring to Figure 8.18, 8.20, or 8.21.

■ **Solution:** (a) To get to manganese, we cross the following regions of the table, with the results indicated.

Period 1	Fill the 1*s* subshell
Period 2	Fill the 2*s* and 2*p* subshells
Period 3	Fill the 3*s* and 3*p* subshells
Period 4	Fill the 4s and then move 5 places in the 3*d* region

The electron configuration of Mn is therefore

$$\text{Mn} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$$

This configuration is correct as is. However, in elements with electrons in *d* and *f* orbitals, we can also group all subshells of the same shell together. For manganese, this gives

$$\text{Mn} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$$

We'll see later that writing the configuration in shell number order is convenient when working out ground state electronic configurations for ions.

(b) To get to bismuth, we fill the following subshells:

Period 1	Fill the 1*s*
Period 2	Fill the 2*s* and 2*p*
Period 3	Fill the 3*s* and 3*p*
Period 4	Fill the 4*s*, 3*d*, and 4*p*
Period 5	Fill the 5*s*, 4*d*, and 5*p*
Period 6	Fill the 6*s*, 4*f*, 5*d*, and then add 3 electrons to the 6*p*

This gives

$$\text{Bi} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^3$$

Grouping subshells with the same value of *n* gives

$$\text{Bi} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$$

Again, either of these configurations is correct.

■ **Is the Answer Reasonable?** We can count the number of electrons to be sure we have 25 for Mn and 83 for Bi and none have been left out or added. Also, we can look at Appendix C.1 to check our configurations.

Practice Exercises

8.8 | Use the periodic table to predict the electron configurations of (a) Mg, (b) Ge, (c) Cd, and (d) Gd. Group subshells of the same shell together. (*Hint*: Recall which areas of the periodic table represent *s*, *p*, *d*, and *f* electrons.)

8.9 | Describe in your own words how to use the periodic table to write the electron configuration of an element.

8.10 | Use the periodic table to predict the electron configurations of (a) O, S, Se and (b) P, N, Sb. What is the same about all the elements in (a), all the elements in (b)?

8.11 | Draw orbital diagrams for (a) Na, (b) S, and (c) Fe. (*Hint:* Recall how we indicate paired electron spins.)

8.12 | Use orbital diagrams to determine how many unpaired electrons are in each of the elements (a) Mg, (b) Ge, (c) Cd, and (d) Gd.

Abbreviated Electron Configurations

It makes sense that when two atoms come together to form new chemical bonds, it must be due to the interactions of the electrons furthest from the nucleus. It also makes sense that electrons buried deep within the atomic structure most likely do not contribute significantly to the chemical properties of an atom. To emphasize and examine the nature of the electrons that are important for chemical reactions and properties, chemists often write **abbreviated electron configurations** (also called shorthand configurations).

When writing an abbreviated electron configuration for any element, Pb for example, the complete electron configuration is divided into two groups as shown below. The first group is represented by the symbol for the noble gas immediately preceding Pb in the periodic table—that is, [Xe]. The second group consists of the remaining electron configuration.

$$\text{Pb} \qquad \underbrace{1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6}_{[\text{Xe}]}\,6s^24f^{14}5d^{10}6p^2$$

$$\text{Pb} \qquad [\text{Xe}] \qquad 6s^24f^{14}5d^{10}6p^2$$

The abbreviated electron configuration is often rearranged in the order of shell numbers.

$$\text{Pb} \qquad [\text{Xe}]\ 4f^{14}5d^{10}6s^26p^2$$

Some simple abbreviated electron configurations can be written for the representative elements sodium and magnesium. The complete electron configuration and the abbreviated configuration are shown below.

Na $1s^22s^22p^63s^1$ Na [Ne] $3s^1$
Mg $1s^22s^22p^63s^2$ Mg [Ne] $3s^2$

The complete and abbreviated electron configurations for a transition element such as iron are

Fe $1s^22s^22p^63s^23p^64s^23d^6$ Fe [Ar] $4s^23d^6$

In addition, the abbreviated electron configurations for Mn and Bi that we worked with in Example 8.4 are

Mn [Ar] $4s^23d^5$ and Bi [Xe] $6s^24f^{14}5d^{10}6p^3$

We can also write the configurations in order of shell numbers, n, as

$$\text{Mn} \quad [\text{Ar}]\ 3d^5 4s^2 \qquad \text{and} \qquad \text{Bi} \quad [\text{Xe}]\ 4f^{14} 5d^{10} 6s^2 6p^3$$

The discussion of valence shell electron configurations that follows illustrates how the abbreviated electron configuration, arranged in shell number order, helps emphasize the electrons that are of most interest with respect to chemical properties.

Example 8.5
Writing Shorthand Electron Configurations

What is the shorthand electron configuration of manganese? Draw the orbital diagram for manganese based on this shorthand configuration. Is manganese paramagnetic or diamagnetic?

■ **Analysis:** This is the same as the previous example except that we list only the electrons in Period 4, while the remaining electrons are represented by the symbol for the appropriate noble gas in square brackets.

■ **Assembling the Tools:** We will need the periodic table, the methods for drawing orbital diagrams, and the conditions that make an element paramagnetic (page 328).

■ **Solution:** Manganese is in Period 4. The preceding noble gas is argon, Ar, in Period 3. To write the abbreviated configuration we write the symbol for argon in brackets followed by the electron configuration that exists beyond argon. We can obtain this by noting that to get to Mn in Period 4, we first cross the "s region" by adding two electrons to the $4s$ subshell, and then go five steps into the "d region" where we add five electrons to the $3d$ subshell. Therefore, the shorthand electron configuration for Mn is

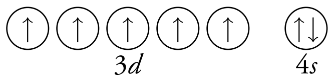
$$\text{Mn} \qquad [\text{Ar}]\ 4s^2 3d^5$$

Placing the electrons that are in the highest shell farthest to the right gives

$$\text{Mn} \qquad [\text{Ar}]\ 3d^5 4s^2$$

To draw the orbital diagram, we simply distribute the electrons in the $3d$ and $4s$ orbitals following Hund's rule. This gives

Mn [Ar]



Each of the $3d$ orbitals is half-filled. The atom contains five unpaired electrons and is paramagnetic.

■ **Is the Answer Reasonable?** From the left end of Period 4, count the groups needed to reach Mn. These should equal 7, the number of electrons in the orbitals beyond Ar as written above. The orbital diagram must have 7 electrons and must obey Hund's rule.

Practice Exercises

8.13 | Can an element with an even atomic number be paramagnetic? (*Hint:* Try writing the orbital diagrams of a few of the transition elements in Period 4.)

8.14 | Write shorthand configurations and abbreviated orbital diagrams for (a) P and (b) Sn. Where appropriate, place the electrons that are in the highest shell farthest to the right. How many unpaired electrons does each of these atoms have?

Valence Shell Electron Configurations

Each group within the periodic table has elements with similar chemical and physical properties that vary regularly within the group. We are now ready to understand the reason for these similarities in terms of the electronic structures of atoms.

Chemical Properties and Valence Shell Configurations

When we consider the chemical reactions of an atom (particularly one of the representative elements), our attention is usually focused on the distribution of electrons in the **outer shell** of the atom (those electrons where n is the largest). This is because the **outer electrons**, those in the outer shell, are the ones that are exposed to other atoms when the atoms react. (Later we will see that d electrons are also very important in reactions involving the transition elements.) It seems reasonable, therefore, that elements with similar properties should have similar outer shell electron configurations. This is, in fact, exactly what we observe. For example, let's look at the alkali metals of Group 1A. Going by our rules, we obtain the following abbreviated electron configurations and complete electron configurations.

Li	[He] $\mathbf{2s^1}$	or	$1s^2\mathbf{2s^1}$
Na	[Ne] $\mathbf{3s^1}$	or	$1s^22s^22p^6\mathbf{3s^1}$
K	[Ar] $\mathbf{4s^1}$	or	$1s^22s^22p^63s^23p^6\mathbf{4s^1}$
Rb	[Kr] $\mathbf{5s^1}$	or	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6\mathbf{5s^1}$
Cs	[Xe] $\mathbf{6s^1}$	or	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6\mathbf{6s^1}$

The abbreviated electron configuration clearly illustrates the similarities of the outermost electron configurations in these elements. Each of these elements has only one outer shell electron that is in an s subshell (shown in bold, red, type). We know that when they react, the alkali metals each lose one electron to form ions with a charge of 1+. For each, the electron that is lost is this outer s electron, and the electron configuration of the ion that is formed is the same as that of the preceding noble gas.

$\mathrm{Li^+}$	$1s^2$	He	$1s^2$
$\mathrm{Na^+}$	$1s^22s^22p^6$	Ne	$1s^22s^22p^6$
$\mathrm{K^+}$	$1s^22s^22p^63s^23p^6$	Ar	$1s^22s^22p^63s^23p^6$

etc.

If you write the abbreviated electron configurations of the members of any of the groups in the periodic table, you will find the same kind of similarity among the configurations of the outer shell electrons. The differences are in the value of the principal quantum number of these outer electrons.

For the representative elements (those in the longer columns), the only electrons that are normally important in controlling chemical properties are the ones in the outer shell. This outer shell is known as the **valence shell**, and it is always the occupied shell with the largest value of n. The electrons in the valence shell are called **valence electrons**. (The term *valence* comes from the study of chemical bonding and relates to the combining capacity of an element, but that's not important here.)

TOOLS

Periodic table and chemical properties

For the representative elements it is very easy to determine the electron configuration of the valence shell by using the periodic table. *The valence shell always consists of just the* s *and* p *subshells that we encounter crossing the period that contains the element in question.* Thus, to determine the valence shell configuration of sulfur, a Period 3 element, we note that to reach sulfur in Period 3 we need to place two electrons into the $3s$ and four electrons into the $3p$ subshells. The valence shell configuration of sulfur is therefore

$$\mathrm{S} \qquad 3s^23p^4$$

and we can say that sulfur has six valence electrons.

Example 8.6
Writing Valence Shell Configurations

Predict the electron configuration of the valence shell of arsenic ($Z = 33$).

Analysis: To determine the number of *s* and *p* electrons in the highest shell, we write the electron configuration grouping the subshells in each shell together.

Assembling the Tools: Our tools are the periodic table and the definition of valence shell electrons.

Solution: To reach arsenic in Period 4, we add electrons to the 4*s*, 3*d*, and 4*p* subshells. However, the 3*d* is not part of the fourth shell and therefore not part of the valence shell, so all we need be concerned with are the electrons in the 4*s* and 4*p* subshells. This gives us the valence shell configuration of arsenic,

$$\text{As} \qquad 4s^2 4p^3$$

Is the Answer Reasonable? We can check that only *s* and *p* electrons are counted and that there are five valence electrons. The answer does seem reasonable.

Practice Exercises

8.15 | Give an example of a valence shell with more than eight electrons. If that is not possible, explain why. (*Hint:* Are there any elements in which the highest numbered *d* subshell electrons are equal to the highest numbered *s* or *p* shell electrons?)

8.16 | What is the valence shell electron configuration of (a) Se, (b) Sn, and (c) I? How many valence electrons do each of these elements have?

Some Unexpected Electron Configurations

The rules you've learned for predicting electron configurations work most of the time, but not always. Appendix C.1 gives the electron configurations of all of the elements as determined experimentally. Close examination reveals that there are quite a few exceptions to the rules. Some of these exceptions are important to us because they occur with common elements.

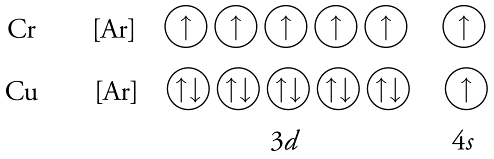
Two important exceptions are for chromium and copper. Following the rules, we would expect the configurations of chromium and copper to be

$$\text{Cr} \qquad [\text{Ar}]\ 3d^4 4s^2$$
$$\text{Cu} \qquad [\text{Ar}]\ 3d^9 4s^2$$

However, the actual electron configurations, determined experimentally, are

$$\text{Cr} \qquad [\text{Ar}]\ 3d^5 4s^1$$
$$\text{Cu} \qquad [\text{Ar}]\ 3d^{10} 4s^1$$

The corresponding orbital diagrams are



Notice that for chromium, an electron is "borrowed" from the 4*s* subshell to give a 3*d* subshell that is exactly half-filled. For copper the 4*s* electron is borrowed to give a completely filled $3d$ subshell. A similar thing happens with silver and gold, which have filled $4d$ and $5d$ subshells, respectively.

Ag $[Kr]\ 4d^{10}5s^1$
Au $[Xe]\ 4f^{14}5d^{10}6s^1$

Apparently, half-filled and filled *d* subshells (particularly the latter) have some special stability that makes such borrowing energetically favorable. This subtle but nevertheless important phenomenon affects not only the ground state configurations of atoms but also the relative stabilities of some of the ions formed by the transition elements. Similar irregularities occur among the lanthanide and actinide elements.

8.9 | Atomic Orbitals: Shapes and Orientations

To picture what electrons are doing within the atom, we are faced with imagining an object that behaves like a particle in some experiments and like a wave in others. There is nothing in our worldly experience that is comparable. Fortunately we can still think of the electron as a particle in the usual sense by speaking in terms of the statistical probability of the electron being found at a particular place. We can then use quantum mechanics to mathematically connect the particle and wave representations of the electron. Even though we may have trouble imagining an object that can be represented both ways, mathematics describes its behavior very accurately.

Describing the electron's position in terms of statistical probability is based on more than simple convenience. The German physicist Werner Heisenberg showed mathematically that it is impossible to measure with complete precision both a particle's velocity and position at the same instant. To measure an electron's position or velocity, we have to bounce another particle, such as a photon, off it. Thus, the very act of making the measurement alters the electron's position and velocity. We cannot determine both exact position and exact velocity simultaneously, no matter how cleverly we make the measurements. This is the Heisenberg **uncertainty principle**. The theoretical limitations on measuring speed and position are not significant for large objects. However, for small particles such as the electron, these limitations prevent us from ever knowing or predicting where in an atom an electron will be at a particular instant, so we speak of probabilities instead.

■ The uncertainty principle is often stated mathematically as

$$\Delta x = \frac{h}{4\pi m}\left(\frac{1}{\Delta v}\right)$$

where Δx is the minimum uncertainty in the particle's location, h is Planck's constant, m is the mass of the particle, and Δv is the minimum uncertainty in the particle's velocity. Notice that we can generally measure the particle's location more precisely if the particle is heavier. Notice also that the greater the uncertainty in the velocity, the smaller the uncertainty in the particle's location.

Wave mechanics views the probability of finding an electron at a given point in space as equal to the square of the amplitude of the electron wave (given by the square of the wave function, ψ^2) at that point. It seems quite reasonable to relate probability to amplitude, or intensity, because where a wave is intense its presence is strongly felt. The amplitude is squared because, mathematically, the amplitude can be either positive or negative, but probability only makes sense if it is positive. Squaring the amplitude assures us that the probabilities will be positive. We need not be very concerned about this point, however.

■ The amplitude of an electron wave is described by a **wave function**, which is usually given the symbol ψ (the Greek letter psi). The probability of finding the electron in a given location is given by ψ^2. The sign of the wave function is important when they are combined, as we discuss in Chapter 10.

The notion of electron probability leads to three very important and frequently used concepts. One is that an electron behaves as if it were spread out around the nucleus in a sort of **electron cloud.** Figure 8.22*a* is a *dot-density diagram* that illustrates the way the probability of finding the electron varies in space for a 1*s* orbital. In those places where the dot density is large (i.e., where there are large numbers of dots per unit volume), the amplitude of the wave is large and the probability of finding the electron is also large.

The second important concept that stems from the notion that the electron probability varies from place to place is **electron density**, which relates to how much of the electron's charge is packed into a given region of space. In regions of high probability there is a high concentration of electrical charge (and mass) and the electron density is large; in regions of low probability, the electron density is small. Figure 8.22*b* shows how the electron probability for a 1*s* orbital varies as we move away from the nucleus. As you might expect, the

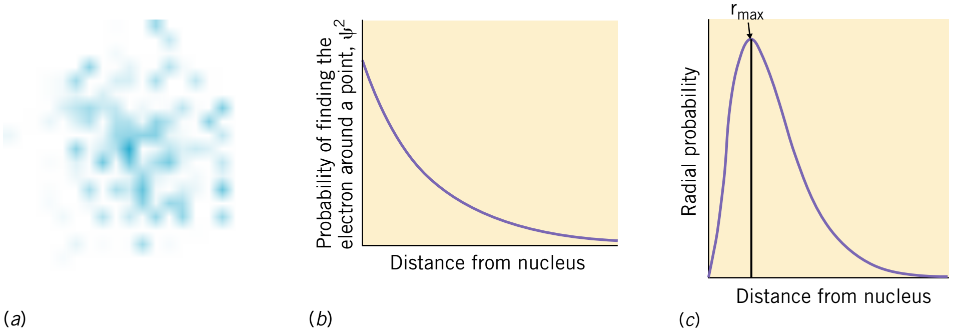


Figure 8.22 | **Electron distribution in the 1*s* orbital of a hydrogen atom.** (*a*) A dot-density diagram that illustrates the electron probability distribution for a 1*s* electron. (*b*) A graph that shows how the probability of finding the 1*s* electron around a given point, ψ^2, decreases as the distance from the nucleus increases. (*c*) A graph of the radial probability distribution of a 1*s* electron that shows the probability of finding the 1*s* electron in a volume between r and $r + x$ from the nucleus. The maximum is the same as the Bohr radius.

probability of finding the electron close to the nucleus is large and decreases with increasing distance from the nucleus.

In a third view we ask ourselves, "What is the probability that an electron will occupy a thin spherical shell from r to $r + x$, where x is very small, away from the nucleus?" If we plot the probabilities for these shells, the graph that we get looks like Figure 8.22*c*. This is called a radial distribution plot. Interestingly, the maximum for such a plot for the hydrogen atom falls precisely at 53 pm, the Bohr radius.

Remember that an electron confined to a tiny space no longer behaves much like a particle. It's more like a cloud of negative charge. Like clouds made of water vapor, the density of the cloud varies from place to place. In some places the cloud is dense; in others the cloud is thinner and may be entirely absent. This is a useful picture to keep in mind as you try to visualize the shapes of atomic orbitals.

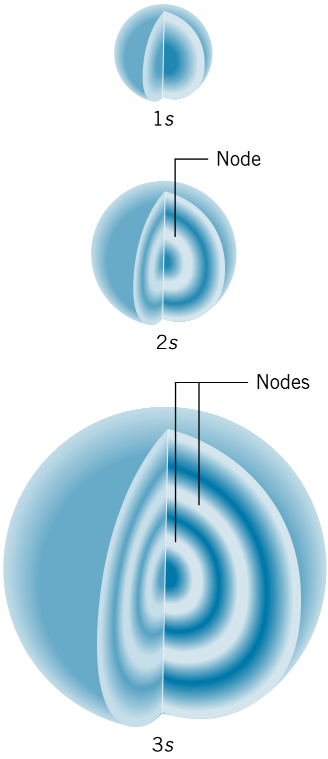


Figure 8.23 | **Size variations among *s* orbitals.** The orbitals become larger as the principal quantum number, *n*, becomes larger.

Shapes and Sizes of *s* and *p* Orbitals

In looking at the way the electron density distributes itself in atomic orbitals, we are interested in three things—the *shape* of the orbital, its *size,* and its *orientation* in space relative to other orbitals.

The electron density in an orbital doesn't end abruptly at some particular distance from the nucleus. It gradually fades away. Therefore, to define the size and shape of an orbital, it is useful to picture some imaginary surface enclosing, say, 90% of the electron density of the orbital, and on which the probability of finding the electron is everywhere the same. For the 1*s* orbital in Figure 8.22, we find that if we go out a given distance from the nucleus in *any* direction, the probability of finding the electron is the same. This means that all the points of equal probability lie on the surface of a sphere, so we can say that the shape of the orbital is spherical. In fact, all *s* orbitals are spherical. As suggested earlier, their sizes increase with increasing *n*. This is illustrated in Figure 8.23. Notice that beginning with the 2*s* orbital, there are certain places where the electron density drops to zero. These are spherically shaped nodes of the *s* orbital electron waves. It is interesting that electron waves have nodes just like the waves on a guitar string. For *s* orbital electron waves, however, the nodes consist of imaginary spherical *surfaces* on which the electron density is zero.

The *p* orbitals are quite different from *s* orbitals, as shown in Figure 8.24. Notice that the electron density is equally distributed in two regions on opposite sides of the nucleus. Figure 8.24*a* illustrates the two "lobes" of *a single* 2*p* orbital. Between the lobes is a **nodal plane**—an imaginary flat surface on which every point has an electron density of zero. The

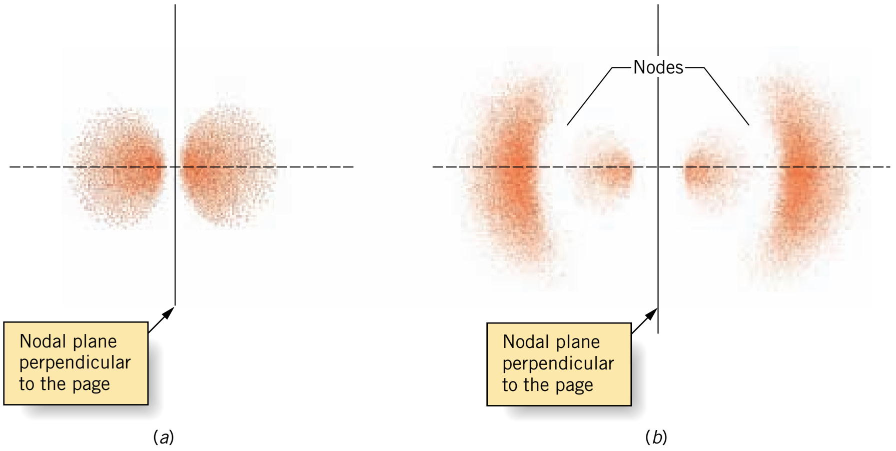

Nodes
Nodal plane perpendicular to the page
Nodal plane perpendicular to the page
(a)
(b)

Figure 8.24 | **Distribution of electron density in *p* orbitals.** (*a*) Dot-density diagram that represents a cross section of the probability distribution in a $2p$ orbital. There is a nodal plane between the two lobes of the orbital. (*b*) Cross section of a $3p$ orbital. Note the nodes in the electron density that are in addition to the nodal plane passing through the nucleus.

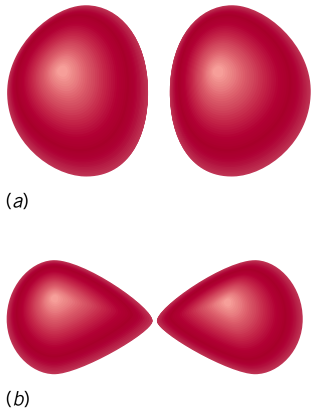


Figure 8.25 | **Representations of the shapes of *p* orbitals.** (*a*) Shape of a surface of constant probability for a $2p$ orbital. (*b*) A simplified representation of a *p* orbital that emphasizes the directional nature of the orbital.

size of the *p* orbitals also increases with increasing *n* as illustrated by the cross section of a $3p$ orbital in Figure 8.24*b*. The $3p$ and higher *p* orbitals have additional nodes besides the nodal plane that passes through the nucleus.

Figure 8.25*a* illustrates the shape of a surface of constant probability for a $2p$ orbital. Often chemists will simplify this shape by drawing two "balloons" connected at the nucleus and pointing in opposite directions as shown in Figure 8.25*b*. Both representations emphasize the point that a *p* orbital has two equal-sized lobes that extend in opposite directions along a line that passes through the nucleus.

Orientations of *p* Orbitals

As you've learned, a *p* subshell consists of three orbitals of equal energy. Wave mechanics tells us that the lines along which the orbitals have their maximum electron densities are oriented at 90° angles to each other, corresponding to the axes of an imaginary *xyz* coordinate system (Figure 8.26). For convenience in referring to the individual *p* orbitals they are often labeled according to the axis along which they lie. The *p* orbital concentrated along the *x* axis is labeled p_x, and so forth.

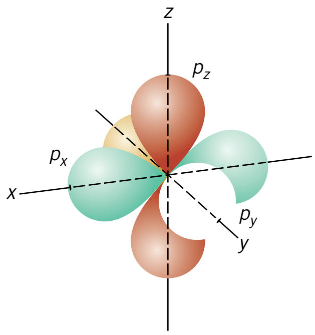


Figure 8.26 | **The orientations of the three *p* orbitals in a *p* subshell.** Because the directions of maximum electron density lie along lines that are mutually perpendicular, like the axes of an *xyz* coordinate system, it is convenient to label the orbitals p_x, p_y, and p_z.

Shapes and Orientations of *d* Orbitals in a *d* Subshell

The shapes of the *d* orbitals, illustrated in Figure 8.27, are a bit more complex than are those of the *p* orbitals. For clarity we do not attempt to draw all five *d* orbitals at the same time on the same set of coordinate axes as we did for the *p* orbitals. Notice that four of the five *d* orbitals have the same shape and consist of four lobes of electron density. These four *d*

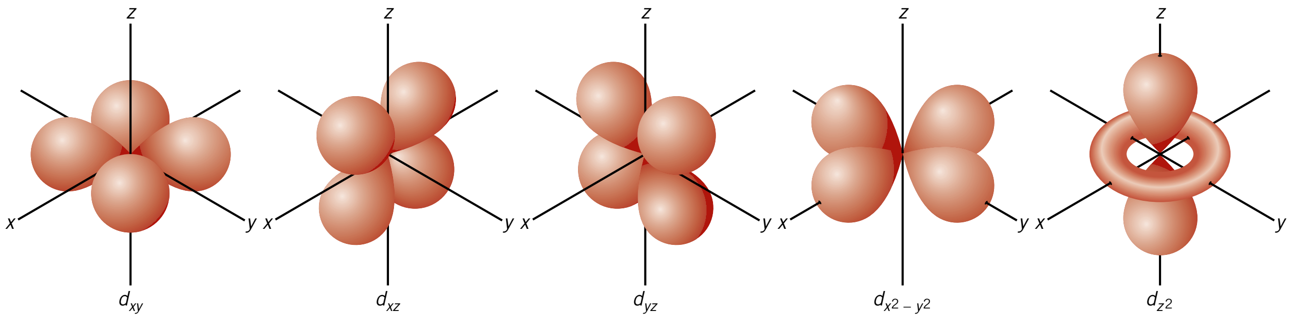


Figure 8.27 | **The shapes and directional properties of the five orbitals of a *d* subshell.**

orbitals each have two perpendicular nodal planes that intersect at the nucleus. These orbitals differ only in their orientations around the nucleus (their labels come from the mathematics of wave mechanics). The fifth *d* orbital, labeled d_{z^2}, has two lobes that point in opposite directions along the *z* axis plus a doughnut-shaped ring of electron density around the center that lies in the *x–y* plane. The two nodes for the d_{z^2} orbital are conic surfaces whose peaks meet at the nucleus. We will see that the *d* orbitals are important in the formation of chemical bonds in certain molecules, and that their shapes and orientations are important in understanding the properties of the transition metals, which we will discuss in Chapter 22.

The shapes of the *f* orbitals are more complex than the *d* orbitals, having more lobes, nodes, and a variety of shapes. Use of *f* orbitals for bonding is not important for this course. However, we should note that each *f* orbital has three nodal planes.

■ The *f* orbitals are even more complex than the *d* orbitals, but we will have no need to discuss their shapes.

8.10 | Periodic Table and Properties of the Elements

There are many chemical and physical properties that vary in a more or less systematic way according to an element's position in the periodic table. For example, in Chapter 3 we noted that the metallic character of the elements increases from top to bottom in a group and decreases from left to right across a period. In this section we discuss several physical properties of the elements that have an important influence on chemical properties. We will see how these properties correlate with an atom's electron configuration, and because electron configuration is also related to the location of an element in the periodic table, we will study their periodic variations as well.

Effective Nuclear Charge

Many of an atom's properties are determined by the amount of positive charge felt by the atom's outer electrons. Except for hydrogen, this positive charge is always *less* than the full nuclear charge, because the negative charge of the electrons in inner shells partially offsets, or "neutralizes," the positive charge of the nucleus.

To gain a better understanding of this, consider the element lithium, which has the electron configuration $1s^22s^1$. The **core electrons** ($1s^2$), which lie beneath the valence shell ($2s^1$), are tightly packed around the nucleus and for the most part lie between the nucleus and the electron in the outer shell. This core has a charge of $2-$ and it surrounds a nucleus that has a charge of $3+$. When the outer $2s$ electron "looks toward" the center of the atom, it "sees" the $3+$ charge of the nucleus reduced to only about $1+$ because of the intervening $2-$ charge of the core. In other words, the $2-$ charge of the core effectively neutralizes two of the positive charges of the nucleus, so the net charge that the outer electron feels, which we call the **effective nuclear charge**, is only about $1+$. This is illustrated in an overly simplified way in Figure 8.28.

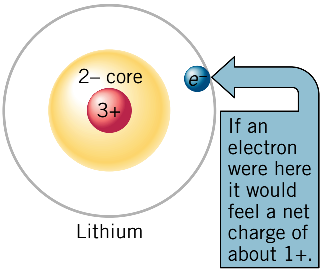

2– core
3+
e−
If an electron were here it would feel a net charge of about 1+.
Lithium

Figure 8.28 | **Effective nuclear charge.** If the $2-$ charge of the $1s^2$ core of lithium were 100% effective at shielding the $2s$ electron from the nucleus, the valence electron would feel an effective nuclear charge of only about $1+$.

Although electrons in inner shells shield the electrons in outer shells quite effectively from the nuclear charge, electrons in the *same* shell are much less effective at shielding each other. For example, in the element beryllium ($1s^22s^2$) each of the electrons in the outer $2s$ orbital is shielded quite well from the nuclear charge by the inner $1s^2$ core, but one $2s$ electron doesn't shield the other $2s$ electron very well at all. This is because electrons in the same shell are at about the same average distance from the nucleus, and in attempting to stay away from each other they only spend a very small amount of time one below the other, which is what's needed to provide shielding. Since electrons in the same shell hardly shield each other at all from the nuclear charge, *the effective nuclear charge felt by the outer electrons is determined primarily by the difference between the charge on the nucleus and the charge on the core.* With this as background, let's examine some properties controlled by the effective nuclear charge.

■ The inner electrons partially shield the outer electrons from the nucleus, so the outer electrons "feel" only a fraction of the full nuclear charge.

■ An electron spends very little time between the nucleus and another electron in the same shell, so it shields that other electron poorly.

Atomic and Ionic Sizes

The wave nature of the electron makes it difficult to define exactly what we mean by the "size" of an atom or ion. As we've seen, the electron cloud doesn't simply stop at some particular distance from the nucleus; instead it gradually fades away. Nevertheless, atoms and ions do behave in many ways as though they have characteristic sizes. For example, in a whole host of hydrocarbons, ranging from methane (CH_4, natural gas) to octane (C_8H_{18}, in gasoline) to many others, the distance between the nuclei of carbon and hydrogen atoms is virtually the same. This would suggest that carbon and hydrogen have the same relative sizes in each of these compounds.

■ The C—H distance in most hydrocarbons is about 110 pm (110×10^{-12} m).

Experimental measurements reveal that the diameters of atoms range from about 1.4×10^{-10} to 5.7×10^{-10} m. Their radii, which is the usual way that size is specified, range from about 7.0×10^{-11} to 2.9×10^{-10} m. Such small numbers are difficult to comprehend. A million carbon atoms placed side by side in a line would extend a little less than 0.2 mm, or about the diameter of the period at the end of this sentence.

The sizes of atoms and ions are rarely expressed in meters because the numbers are so cumbersome. Instead, a unit is chosen that makes the values easier to comprehend. A unit that scientists have traditionally used is called the **angstrom** (symbolized **Å**), which is defined as

$$1\ \text{Å} = 1 \times 10^{-10}\ \text{m}$$

However, the angstrom is not an SI unit, and in many current scientific journals, atomic dimensions are given in picometers, or sometimes in nanometers ($1\ \text{pm} = 10^{-12}$ m and $1\ \text{nm} = 10^{-9}$ m). In this book, we will normally express atomic dimensions in picometers, but because much of the scientific literature has these quantities in angstroms, you may someday find it useful to remember the conversions:

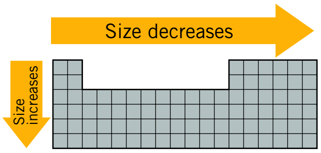
$$1\ \text{Å} = 100\ \text{pm}$$
$$1\ \text{Å} = 0.1\ \text{nm}$$

■ The angstrom is named after Anders Jonas Ångström (1814–1874), a Swedish physicist who was the first to measure the wavelengths of the four most prominent lines of the hydrogen spectrum.

Periodic Variations

The variations in atomic radii within the periodic table are illustrated in Figure 8.29. There we see that atoms generally become larger going from top to bottom in a group, and they become smaller going from left to right across a period. To understand these variations we must consider two factors. One is the value of the principal quantum number of the valence electrons, and the other is the effective nuclear charge felt by the valence electrons.

■ Large atoms are found in the lower left of the periodic table, and small atoms are found in the upper right.



General variation of atomic size within the periodic table.

TOOLS

Periodic trends in atomic size

Going from top to bottom within a group, the effective nuclear charge felt by the outer electrons remains nearly constant, while the principal quantum number of the valence shell increases. For example, consider the elements of Group 1A. For lithium, the valence shell configuration is $2s^1$; for sodium, it is $3s^1$; for potassium, it is $4s^1$; and so forth. For each of these elements, the core has a negative charge that is one less than the nuclear charge, so the valence electron of each experiences a nearly constant effective nuclear charge of about 1+. However, as we descend the group, the value of n for the valence shell increases, and as you learned in Section 8.5, the larger the value of n, the larger the orbital. Therefore, the atoms become larger as we go down a group simply because the orbitals containing the valence electrons become larger. This same argument applies whether the valence shell orbitals are s or p.

Moving from left to right across a period, electrons are added to the same shell. The orbitals holding the valence electrons all have the *same* value of n. In this case we have to examine the variation in the effective nuclear charge felt by the valence electrons.

As we move from left to right across a period, the nuclear charge increases, and the outer shells of the atoms become more populated but the inner core remains the same. For example, from lithium to fluorine the nuclear charge increases from 3+ to 9+. The core ($1s^2$) stays the same, however. As a result, the outer electrons feel an increase in positive charge (i.e., effective nuclear charge), which causes them to be drawn inward and thereby causes the sizes of the atoms to decrease.

Across a row of transition elements or inner transition elements, the size variations are less pronounced than among the representative elements. This is because the outer shell configuration remains essentially the same while an inner shell is filled. From atomic numbers 21 to 30, for example, the outer electrons occupy the $4s$ subshell while the underlying $3d$ subshell is gradually completed. The amount of shielding provided by the addition of electrons to this inner $3d$ level is greater than the amount of shielding that would occur if the electrons were added to the outer shell, so the effective nuclear charge felt by the outer

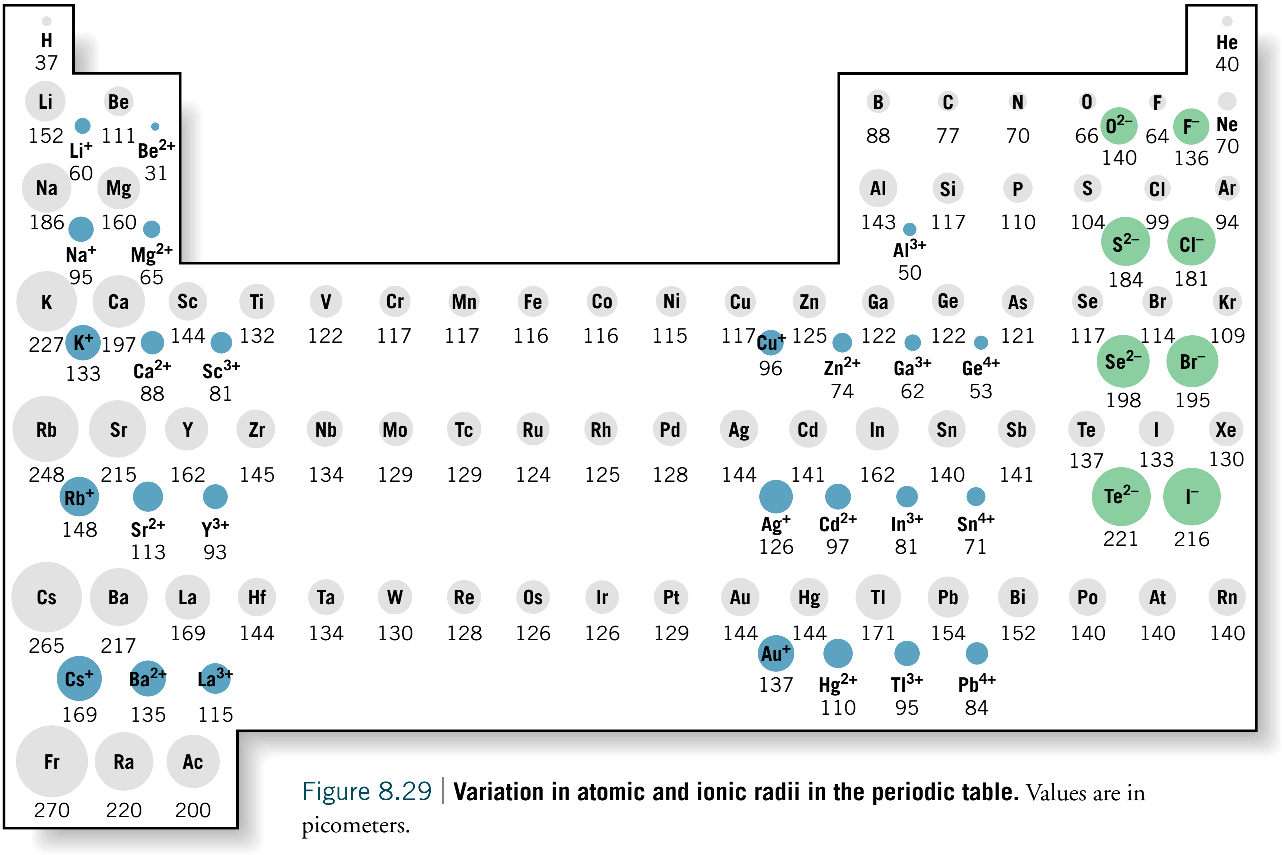

H
37
He
40
Li
152
Li^+
60
Be
111
Be^{2+}
31
B
88
C
77
N
70
O
66
O^{2-}
140
F
64
F^-
136
Ne
70
Na
186
Na^+
95
Mg
160
Mg^{2+}
65
Al
143
Al^{3+}
50
Si
117
P
110
S
104
S^{2-}
184
Cl
99
Cl^-
181
Ar
94
K
227
K^+
133
Ca
197
Ca^{2+}
88
Sc
144
Sc^{3+}
81
Ti
132
V
122
Cr
117
Mn
117
Fe
116
Co
116
Ni
115
Cu
117
Cu^+
96
Zn
125
Zn^{2+}
74
Ga
122
Ga^{3+}
62
Ge
122
Ge^{4+}
53
As
121
Se
117
Se^{2-}
198
Br
114
Br^-
195
Kr
109
Rb
248
Rb^+
148
Sr
215
Sr^{2+}
113
Y
162
Y^{3+}
93
Zr
145
Nb
134
Mo
129
Tc
129
Ru
124
Rh
125
Pd
128
Ag
144
Ag^+
126
Cd
141
Cd^{2+}
97
In
162
In^{3+}
81
Sn
140
Sn^{4+}
71
Sb
141
Te
137
Te^{2-}
221
I
133
I^-
216
Xe
130
Cs
265
Cs^+
169
Ba
217
Ba^{2+}
135
La
169
La^{3+}
115
Hf
144
Ta
134
W
130
Re
128
Os
126
Ir
126
Pt
129
Au
144
Au^+
137
Hg
144
Hg^{2+}
110
Tl
171
Tl^{3+}
95
Pb
154
Pb^{4+}
84
Bi
152
Po
140
At
140
Rn
140
Fr
270
Ra
220
Ac
200

Figure 8.29 | **Variation in atomic and ionic radii in the periodic table.** Values are in picometers.

electrons increases more gradually. As a result, the decrease in size with increasing atomic number is also more gradual.

Ion Size Compared to Atomic Size

Figure 8.29 also illustrates how sizes of the ions compare with those of the neutral atoms. As you can see, when atoms gain or lose electrons to form ions, rather significant size changes take place. The reasons are easy to understand and remember.

Periodic trends in ionic size

When electrons are added to an atom, the mutual repulsions between them increase. This causes the electrons to push apart and occupy a larger volume. Therefore, *negative ions are often about 1.5 to 2 times larger than the atoms from which they are formed* (Figure 8.30).

When electrons are removed from an atom, the electron–electron repulsions decrease, which allows the remaining electrons to be pulled closer together around the nucleus. Therefore, *positive ions are always smaller than*

■ Adding electrons creates an ion that is larger than the neutral atom; removing electrons produces an ion that is smaller than the neutral atom.

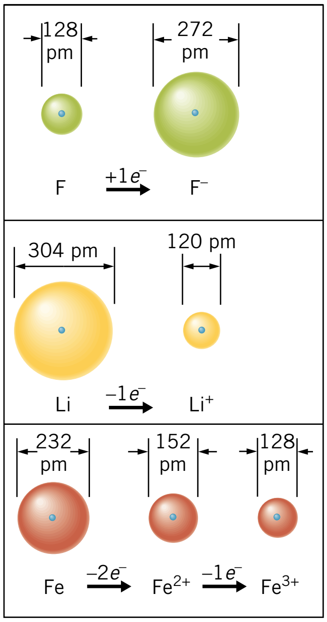

128 pm
272 pm
F
$+1e^-$
F^-
304 pm
120 pm
Li
$-1e^-$
Li^+
232 pm
152 pm
128 pm
Fe
$-2e^-$
Fe^{2+}
$-1e^-$
Fe^{3+}

Figure 8.30 | **Changes in size when atoms gain or lose electrons to form ions.** Adding electrons leads to an increase in the size of the particle, as illustrated for fluorine. Removing electrons leads to a decrease in the size of the particle, as shown for lithium and iron.

the atoms from which they are formed. As Figure 8.29 shows, cations often are only 1/2 to 2/3 the size of their parent atom. This is also illustrated in Figure 8.30 for the elements lithium and iron. For lithium, removal of the outer 2*s* electron completely empties the valence shell and exposes the smaller $1s^2$ core. When a metal is able to form more than one positive ion, the sizes of the ions decrease as the amount of positive charge on the ion increases. To form the Fe^{2+} ion, an iron atom loses its outer 4*s* electrons. To form the Fe^{3+} ion, an additional electron is lost from the 3*d* subshell that lies beneath the 4*s*. Comparing sizes, we see that the radius of an iron atom is 116 pm whereas the radius of the Fe^{2+} ion is 76 pm. Removing yet another electron to give Fe^{3+} decreases electron–electron repulsions in the *d* subshell and gives the Fe^{3+} ion a radius of 64 pm.

- Li $1s^22s^1$
  Li$^+$ $1s^2$

- Fe [Ar] $3d^64s^2$
  Fe^{2+} [Ar] $3d^6$
  Fe^{3+} [Ar] $3d^5$

Practice Exercises

8.17 | Use the periodic table to choose the largest atom or ion in each set.
(a) Ge, Te, Se, Sn (b) C, F, Br, Ga (c) Cr, Cr^{2+}, Cr^{3+} (d) O, O^{2-}, S, S^{2-}
(*Hint:* Recall that electrons repel each other.)

8.18 | Use the periodic table to determine the smallest atom or ion in each group.
(a) Si, Ge, As, P (b) Fe^{2+}, Fe^{3+}, Fe (c) Db, W, Tc, Fe (d) Br^-, I^-, Cl^-

Ionization Energy

The **ionization energy** (abbreviated **IE**) *is the energy required to remove an electron from an isolated, gaseous atom or ion in its ground state.* For an atom of an element *X*, it is the increase in potential energy associated with the change

$$X(g) \longrightarrow X^+(g) + e^-$$

In effect, the ionization energy is a measure of how much work is required to pull an electron from an atom, so it reflects how tightly the electron is held by the atom. Usually, the ionization energy is expressed in units of kilojoules per mole (kJ/mol), so we can also view it as the energy needed to remove one mole of electrons from one mole of gaseous atoms.

Table 8.2 lists the ionization energies of the first 12 elements. As you can see, atoms with more than one electron have more than one ionization energy. These correspond to

Table 8.2 **Successive Ionization Energies in kJ/mol for Hydrogen through Magnesium**

	1st	2nd	3rd	4th	5th	6th	7th	8th
H	1312							
He	2372	5250						
Li	520	7297	11,810					
Be	899	1757	14,845	21,000				
B	800	2426	3659	25,020	32,820			
C	1086	2352	4619	6221	37,820	47,260		
N	1402	2855	4576	7473	9442	53,250	64,340	
O	1314	3388	5296	7467	10,987	13,320	71,320	84,070
F	1680	3375	6045	8408	11,020	15,160	17,860	92,010
Ne	2080	3963	6130	9361	12,180	15,240	—	—
Na	496	4563	6913	9541	13,350	16,600	20,113	25,666
Mg	737	1450	7731	10,545	13,627	17,995	21,700	25,662

Note the sharp increase in ionization energy when crossing the “staircase,” indicating that the last of the valence electrons has been removed.

the stepwise removal of electrons, one after the other. Lithium, for example, has three ionization energies because it has three electrons. Removing the outer $2s$ electrons from one mole of isolated lithium atoms to give one mole of gaseous lithium ions, Li^+, requires 520 kJ; so the *first ionization energy* of lithium is 520 kJ/mol. The second IE of lithium is 7297 kJ/mol, and corresponds to the process

$$Li^+(g) \longrightarrow Li^{2+}(g) + e^-$$

This involves the removal of an electron from the now-exposed $1s$ core of lithium and requires more than thirteen times the energy used to remove the first electron. Removal of the third (and last) electron requires the third IE, which is 11,810 kJ/mol. In general, successive ionization energies always increase because each subsequent electron is being pulled away from an increasingly more positive ion, and that requires more work.

Earlier we saw that the explanation of the photoelectric effect by Einstein led to the concept of light quanta, or photons. This phenomena is used in a powerful research technique called photoelectron spectroscopy that described in *On the Cutting Edge 8.1*.

■ Ionization energies are additive. For example,

$$Li(g) \longrightarrow Li^+(g) + e^- \qquad IE_1 = 520 \text{ kJ}$$

$$Li^+(g) \longrightarrow Li^{2+}(g) + e^- \qquad IE_2 = 7297 \text{ kJ}$$

$$Li(g) \longrightarrow Li^{2+}(g) + 2e^- \qquad IE_{total} = IE_1 + IE_2 = 7817 \text{ kJ}$$

ON THE CUTTING EDGE 8.2

Photoelectron Spectroscopy

The photoelectric effect, where electrons can be ejected from a surface by a beam of light, was described earlier in this chapter. In 1921 Albert Einstein was awarded the Nobel Prize in physics for explaining this phenomenon. To do so he viewed electromagnetic radiation as particles, or photons, with each photon having a quantum of energy equal to its frequency multiplied by Planck's constant, $h\nu$. Einstein then postulated that electrons are attracted to the nucleus with a certain amount of energy that he called the binding energy, BE. He then reasoned that if a photon has more energy than an electron's binding energy, the photon would be able to eject an electron out of the atom. In simpler terms, he showed that it is the energy of the photon that ejects an electron rather than the number of photons.

In addition to the atomic view of the photoelectric process, we know that energy must be conserved. The total energy entering the system is the energy of the photon, $h\nu$. That must exceed the binding energy, BE, and the excess energy appears as the kinetic energy, KE, of the ejected electron.

$$h\nu = BE + KE$$

Researchers can measure the energy of the incoming photon from its frequency and can measure the kinetic energies of the ejected electrons, to determine the binding energies of the ejected electrons. The binding energy is closely related to the ionization energy for a given electron.

In practice, photoelectron spectroscopy, PES, can be divided into two closely related methods. Ultraviolet photoelectron spectroscopy (UPS) uses UV radiation to eject electrons from a sample; X-ray photoelectron spectroscopy, XPS, that uses X rays. In 1981, Kai Siegbahn was awarded the Nobel

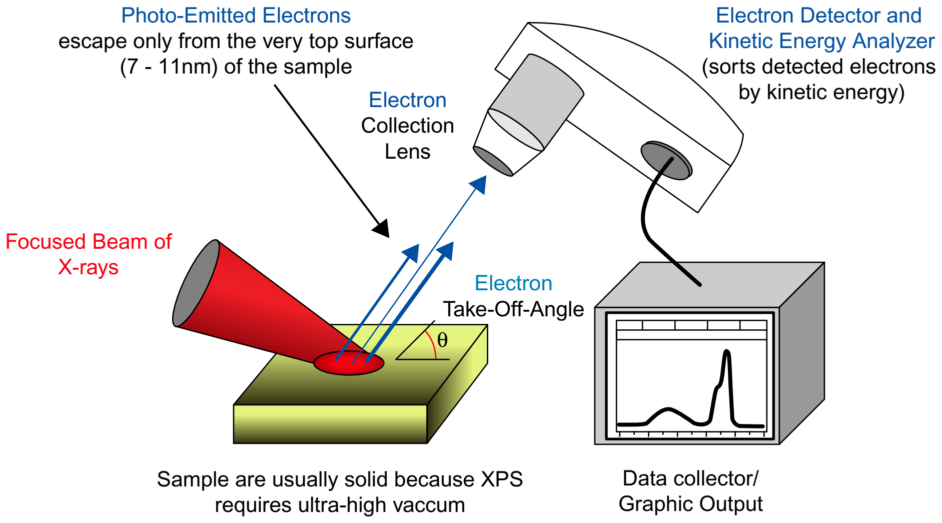


Figure 1 A conceptualized drawing of a photoelectron spectrometer.

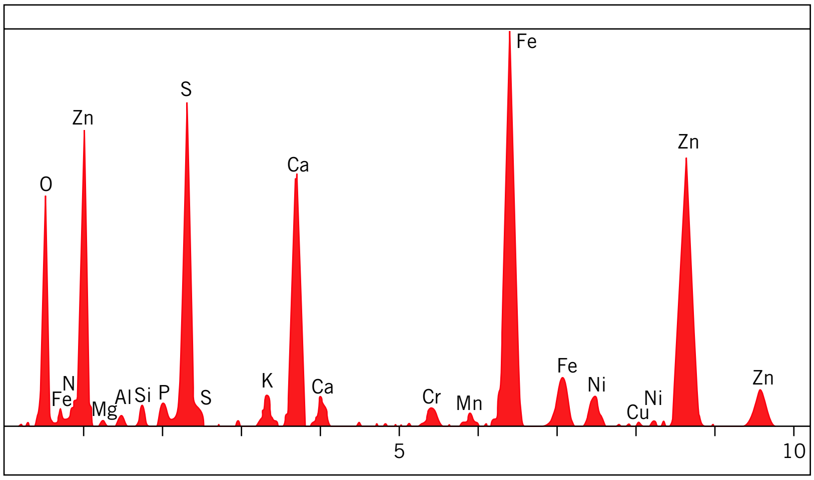


Figure 2 A conceptual graph of intensity versus kinetic energy generated by a PES experiment.

Prize in physics for the use of XPS in chemical analysis. Current research using PES involves chemical analysis, the study of surfaces and molecules that bind to them, and fine details about molecular structure. Under the appropriate conditions, the oxidation state of an atom can be determined based on the observed binding energy.

Instruments used for PES must provide a monochromatic beam (close to a single wavelength) of UV light or X rays. To ensure that the ejected electrons get to the detector before colliding with another molecule, the sample chamber must have an ultra-high vacuum. The ejected electrons then enter a detector that monitors the number and the kinetic energy of the electrons. This information is collected by a computer and may be shown graphically on the computer monitor. See Figure 1.

The typical result of a PES experiment is a plot of the number of electrons versus the kinetic energy of the ejected electrons. Figure 2 illustrates an x-ray PES spectrum used for chemical analysis.

Periodic Trends in IE

Within the periodic table there are trends in the way IE varies that are useful to know and to which we will refer in later discussions. We can see these by examining Figure 8.31 that shows a graph of how the first ionization energy varies with an element's position in the periodic table. Notice that the elements with the largest ionization energies are the nonmetals in the upper right of the periodic table, and that those with the smallest ionization energies are the metals in the lower left of the table. In general, then, the following trends are observed.

> Ionization energy generally increases from bottom to top within a group and increases from left to right within a period. Overall the ionization energy increases from the lower left corner of the periodic table to the upper right corner. This is usually referred to as a **diagonal trend**.

TOOLS

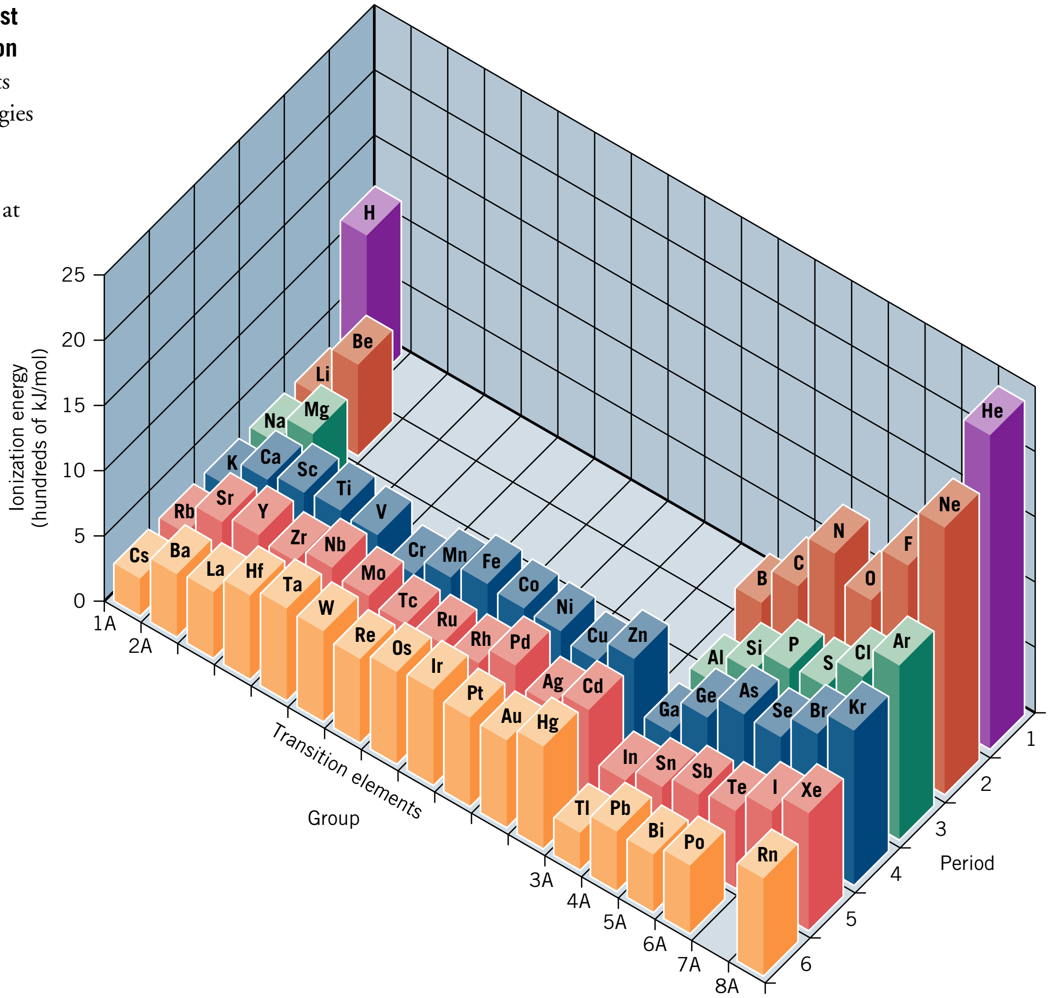
Periodic trends in ionization energy

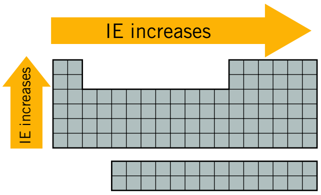
The same factors that affect atomic size also affect ionization energy. As the value of n increases going down a group, the orbitals become larger and the outer electrons are farther from the nucleus. Electrons farther from the nucleus are bound less tightly, so IE decreases from top to bottom.

As you can see, there is a gradual overall increase in IE as we move from left to right across a period, although the horizontal variation of IE is somewhat irregular. The reason for the overall trend is the increase in effective nuclear charge felt by the valence electrons as we move across a period. As we've seen, this draws the valence electrons closer to the nucleus and leads to a decrease in atomic size as we move from left to right. However, the

■ It is often helpful to remember that the trends in IE are just the opposite of the trends in atomic size within the periodic table; when size increases, IE decreases.

Figure 8.31 | **Variation in first ionization energy with location in the periodic table.** Elements with the largest ionization energies are in the upper right of the periodic table. Those with the smallest ionization energies are at the lower left.





General variation of ionization energy (as an exothermic quantity) **within the periodic table.**

increasing effective nuclear charge also causes the valence electrons to be held more tightly, which makes it more difficult to remove them.

The results of these trends place elements with the largest IE in the upper right-hand corner of the periodic table. It is very difficult to cause these atoms to lose electrons. In the lower left-hand corner of the table are elements that have loosely held valence electrons. These elements form positive ions relatively easily, as you learned in Chapter 3.

Stability of Noble Gas Configurations

Table 8.2 shows that, for a given representative element, successive ionization energies increase gradually until the valence shell is emptied. Then a very much larger increase in IE occurs as the core is broken into. This is illustrated graphically in Figure 8.32 for the Period 2 elements lithium through fluorine. For lithium, we see that the first electron (the $2s$ electron) is removed rather easily, but the second and third electrons, which come from the $1s$ core, are much more difficult to dislodge. For beryllium, the large jump in IE occurs after two electrons (the two $2s$ electrons) are removed. In fact, for all of these elements, the large increase in IE happens when the core is broken into.

The data displayed in Figure 8.32 suggest that although it may be moderately difficult to empty the valence shell of an atom, it is *extremely* difficult to break into the noble gas configuration of the core electrons. As you will learn, this is one of the factors that influences the number of positive charges on ions formed by the representative metals.

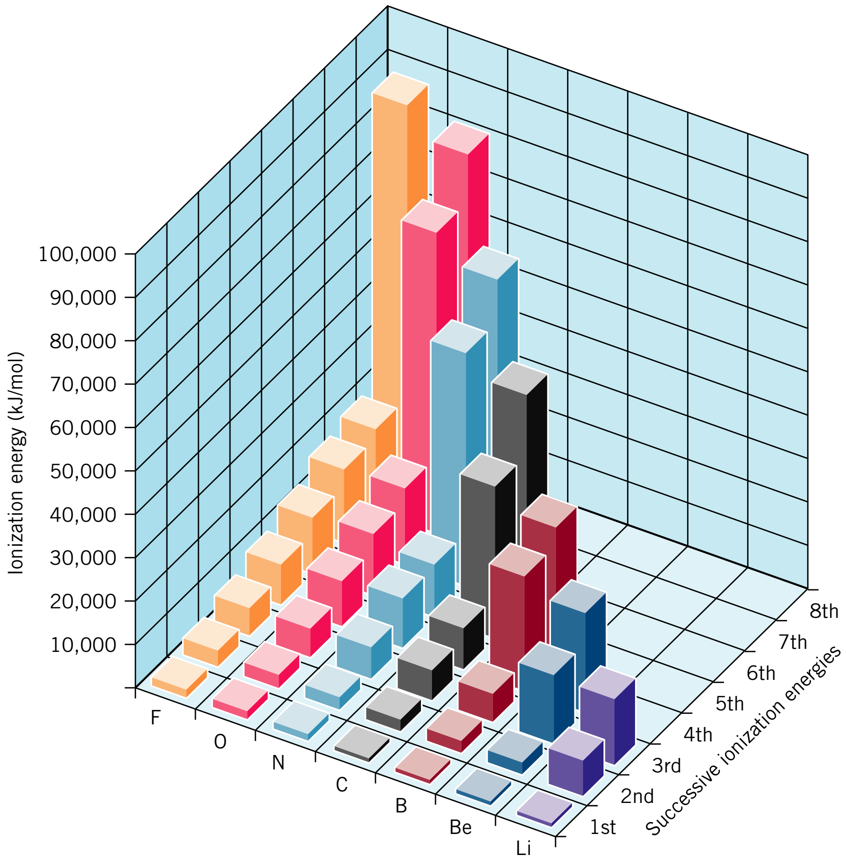


Figure 8.32 | **Variations in successive ionization energies for the elements lithium through fluorine.**

Practice Exercises

8.19 | Use the periodic table to select the atom with the most positive value for its first ionization energy, IE: (a) Na, Sr, Be, Rb; (b) B, Al, C, Si. (*Hint:* Use the diagonal relationships of the IE values within the periodic table.)

8.20 | Use Table 8.2 to determine which of the following elements is expected to have the most positive ionization energy, IE: (a) Na^+, Mg^+, H, C^{2+}; (b) Ne, F, Mg^{2+}, Li^+.

Electron Affinity

The **electron affinity** (abbreviated **EA**) *is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state.* For an element *X*, it is the change in potential energy associated with the process

$$X(g) + e^- \longrightarrow X^-(g)$$

As with ionization energy, electron affinities are usually expressed in units of kilojoules per mole, so we can also view the EA as the energy change associated with adding one mole of electrons to one mole of gaseous atoms or ions.

For nearly all the elements, the addition of one electron to the neutral atom is exothermic, and the EA is given as a negative value. This is because the incoming electron experiences an attraction to the nucleus that causes the potential energy to be lowered as the electron approaches the atom. However, when a second electron must be added, as in the formation of the oxide ion, O^{2-}, work must be done to force the electron into an already negative ion. This is an endothermic process where energy must be added and the EA has a positive value.

Change	**EA (kJ/mol)**
$O(g) + e^- \longrightarrow O^-(g)$	−141
$O^-(g) + e^- \longrightarrow O^{2-}(g)$	+844
$O(g) + 2e^- \longrightarrow O^{2-}(g)$	+703 (net)

Notice that more energy is absorbed adding an electron to the O^- ion than is released by adding an electron to the O atom. Overall, the formation of an isolated oxide ion leads to a net increase in potential energy (so we say its formation is *endothermic*). The same applies to the formation of *any* negative ion with a charge larger than 1−.

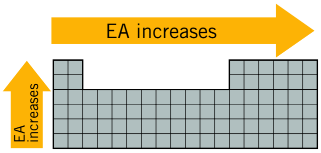
Periodic Variations

The electron affinities of the representative elements are listed in Table 8.3, and we see that periodic trends in electron affinity roughly parallel those for ionization energy.

Periodic trends in electron affinity

> Although there are some irregularities, overall the electron affinities of the elements become more *exothermic* going from left to right across a period and from bottom to top in a group.

This shouldn't be surprising, because a valence shell that loses electrons easily (low IE) will have little attraction for additional electrons (small EA). On the other hand, a valence shell that holds its electrons tightly will also tend to bind an additional electron tightly.



General variation of electron affinity (as an exothermic quantity) **within the periodic table.**

Irregularities in Periodic Trends

As mentioned previously, the variation in first ionization energy across a period is not a smooth one, as seen in the graph in Figure 8.33 for the elements in Period 2. The first irregularity occurs between Be and B, where the IE increases from Li to Be but then decreases from Be to B. This happens because there is a change in the nature of the subshell from which the electron is being removed. For Li and Be, the electron is removed from the 2*s* subshell, but at boron the first electron comes from the higher energy 2*p* subshell where it is not bound so tightly.

Table 8.3 Electron Affinities of the Representative Elements (kJ/mol)

1A	2A	3A	4A	5A	6A	7A
H						
−73						
Li	Be	B	C	N	O	F
−60	+238	−27	−122	~ +9	−141	−328
Na	Mg	Al	Si	P	S	Cl
−53	+230	−44	−134	−72	−200	−348
K	Ca	Ga	Ge	As	Se	Br
−48	+155	−30	−120	−77	−195	−325
Rb	Sr	In	Sn	Sb	Te	I
−47	+167	−30	−121	−101	−190	−295
Cs	Ba	Tl	Pb	Bi	Po	At
−45	+50	−30	−110	−110	−183	−270

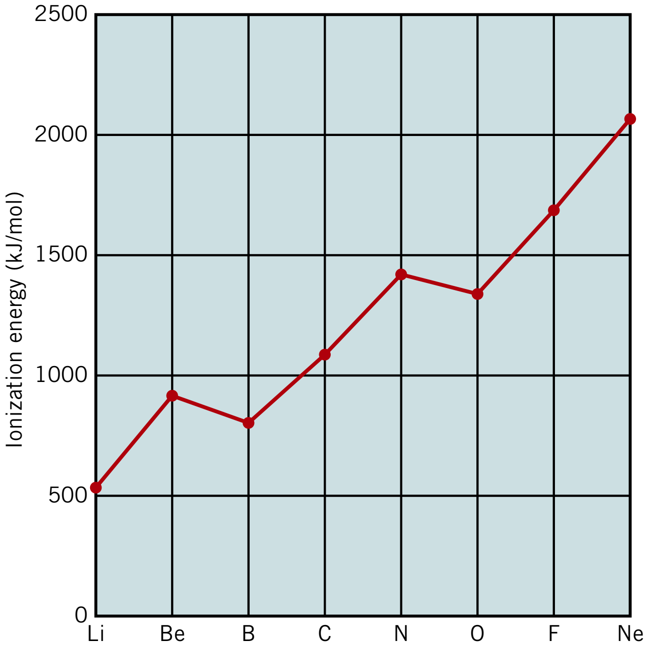
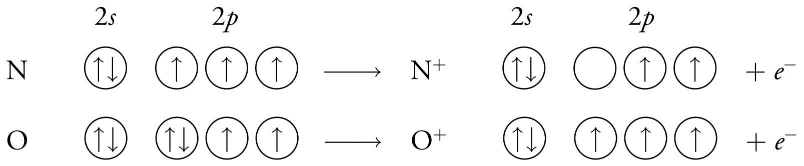


Figure 8.33 | **A closer look at the variation in ionization energy for the Period 2 elements Li through Ne.**

Another irregularity occurs between nitrogen and oxygen. For nitrogen, the electron that's removed comes from a singly occupied orbital. For oxygen, the electron is taken from an orbital that already contains an electron. We can diagram this as follows:



For oxygen, repulsions between the two electrons in the *p* orbital that's about to lose an electron help the electron leave. This "help" is absent for the electron that's about to leave the *p* orbital of nitrogen. As a result, it is not as difficult to remove one electron from an oxygen atom as it is to remove one electron from a nitrogen atom.

As with ionization energy, there are irregularities in the periodic trends for electron affinity. For example, the Group 2A elements have little tendency to acquire electrons because their outer shell *s* orbitals are filled. The incoming electron must enter a higher energy *p* orbital. We also see that the EA for elements in Group 5A are either endothermic or only slightly exothermic. This is because the incoming electron must enter an orbital already occupied by an electron.

One of the most interesting irregularities occurs between Periods 2 and 3 among the nonmetals. In any group, the element in Period 2 has a less exothermic electron affinity than the element below it. The reason seems to be the small size of the nonmetal atoms of Period 2, which are among the smallest elements in the periodic table. Repulsions between the many electrons in the small valence shells of these atoms leads to a lower than expected attraction for an incoming electron and a less exothermic electron affinity than the element below in Period 3.

Summary

Electromagnetic Energy. Electromagnetic energy, or light energy, travels through space at a constant speed of 3.00×10^8 m s^{-1} in the form of waves. The **wavelength**, λ, and **frequency**, ν, of the wave are related by the equation $\lambda\nu = c$, where c is the **speed of light**. The SI unit for frequency is the **hertz** (**Hz**, 1 Hz $= 1$ s^{-1}). Light also behaves as if it consists of small packets of energy called **photons** or **quanta**, based on the **photoelectric effect**. The energy delivered by a photon is proportional to the frequency of the light, and is given by the equation $E = h\nu$, where h is **Planck's constant**. White light is composed of all the frequencies visible to the eye and can be split into a **continuous spectrum**. Visible light represents only a small portion of the entire **electromagnetic spectrum**, which also includes **X rays, ultraviolet, infrared, microwaves**, and **radio** and **TV** waves.

Atomic Spectra. The occurrence of **line spectra** tells us that atoms can emit energy only in discrete amounts and suggests that the energy of the electron is **quantized**; that is, the electron is restricted to certain specific **energy levels** in an atom. Niels Bohr recognized this and, although his theory was later shown to be incorrect, he was the first to propose a model that was able to account for the **Rydberg equation**. Bohr was the first to introduce the idea of **quantum numbers**.

Matter Waves. The wave behavior of electrons and other tiny particles, which can be demonstrated by **diffraction** experiments, was suggested by de Broglie. Schrödinger applied wave theory to the atom and launched the theory we call **wave mechanics** or **quantum mechanics**. This theory tells us that electron waves in atoms are **standing waves** whose crests and **nodes** are stationary. Each standing wave, or **orbital**, is characterized by three quantum numbers, n, ℓ, and m_ℓ (**principal**, **secondary**, and **magnetic quantum numbers**, respectively). **Shells** are designated by n (which can range from 1 to ∞), **subshells** by ℓ (which can range from 0 to $n - 1$), and orbitals within subshells by m_ℓ (which can range from $-\ell$ to $+\ell$).

Electron Configurations. The electron has magnetic properties that are explained in terms of spin. The **spin quantum number**, m_s, can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$. The **Pauli exclusion principle** limits orbitals to a maximum population of two electrons with **paired spins**. Substances with unpaired electrons are **paramagnetic** and are weakly attracted to a magnetic field. Substances with only paired electrons are **diamagnetic** and are slightly repelled by a magnetic field. The **electron configuration** of an element in its **ground state** is obtained by filling orbitals beginning with the 1s subshell and following the Pauli exclusion principle and **Hund's rule** (which states that electrons spread out as much as possible in orbitals of equal energy). The periodic table serves as a guide in predicting electron configurations. **Abbreviated configurations** show subshell populations outside a noble gas **core**. **Valence shell configurations** show the populations of subshells in the **outer shell** of an atom of the representative elements. Sometimes we represent electron configurations using **orbital diagrams**. Unexpected configurations occur for chromium and copper because of the extra stability of half-filled and filled subshells.

Orbital Shapes. The **Heisenberg uncertainty principle** says we cannot know exactly the position and velocity of an electron both at the same instant. Consequently, wave mechanics describes the probable locations of electrons in atoms. In each orbital the electron is conveniently viewed as an **electron cloud** with a varying **electron density**. All s orbitals are spherical; each p orbital consists of two lobes with a **nodal plane** between them. A p subshell has three p orbitals whose axes are mutually perpendicular and point along the x, y, and z axes of an imaginary coordinate system centered at the nucleus. Four of the five d orbitals in a d subshell have the same shape, with four lobes of electron density each. The fifth has two lobes of electron density pointing in opposite directions along the z axis and a ring of electron density in the x–y plane.

Atomic Properties. The amount of positive charge felt by the valence electrons of an atom is the **effective nuclear charge**. This is less than the actual nuclear charge because core electrons partially shield the valence electrons from the full positive charge of the nucleus. **Atomic radii** depend on the value of n of the valence shell orbitals and the effective nuclear charge experienced by the valence electrons. These radii are expressed in units of picometers or nanometers, or an older unit called the **angstrom** (**Å**). 1 Å $=$ 100 pm $=$ 0.1 nm. Atomic radii decrease from left to right in a period and from bottom to top in a group in the periodic table. Negative ions are larger than the atoms from which they are formed; positive ions are smaller than the atoms from which they are formed.

Ionization energy (IE) is the energy needed to remove an electron from an isolated gaseous atom, molecule, or ion in its ground state; it is endothermic. The first ionization energies of the elements increase from left to right in a period and from bottom to top in a group. (Irregularities occur in a period when the nature of the orbital from which the electron is removed changes and when the electron removed is first taken from a doubly occupied p orbital.) Successive ionization energies become larger, but there is a very large jump when the next electron must come from the noble gas core beneath the valence shell.

Electron affinity (EA) is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state. For atoms, the first EA is usually exothermic. When more than one electron is added to an atom, the overall potential energy change is endothermic. In general, electron affinity becomes more exothermic from left to right in a period and from bottom to top in a group. (However, the EA of second period nonmetals is less exothermic than for the nonmetals of the third period. Irregularities across a period occur when the electron being added must enter the next higher-energy subshell and when it must enter a half-filled p subshell.)

Periodic trends are regular changes of properties within the periods and groups of the periodic table. These include the variation of atomic size, ionic size, ionization energy, electron affinity, and effective nuclear charge. Periodic and group trends in properties can often be combined into a **diagonal trend** from the lower left corner (Fr) to the upper right corner (F). Atomic size, ionization energy, and electron affinity can be viewed as diagonal trends.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Wavelength–frequency relationship (page 307)
Use this equation to convert between frequency and wavelength: $\lambda \times \nu = c$

Energy of a photon (page 312)
With this tool you can calculate the energy carried by a photon of frequency ν. Also, ν can be calculated if E is known.

$$E = h\nu = h\frac{c}{\lambda}$$

Rydberg Equation (page 315)
The wavelengths of the emission spectrum of hydrogen are calculated using this equation.

Electron configurations using the periodic table (page 331)
In this chapter you learned to use the periodic table as an aid in writing electron configurations of the elements.

Periodic table and chemical properties (page 335)
Valence electrons define chemical properties of the elements. Elements within a group (family) have similarites in their valence electrons and thus similar chemical properties.

Periodic trends in atomic and ionic size (pages 341 and 342)
We use the periodic table to predict relative sizes of atoms and ions.

Periodic trends in ionization energy (page 345)
This is used to compare the ease with which atoms of the elements lose electrons.

Periodic trends in electron affinity (page 348)
Trends help in comparing the tendency of atoms or ions to gain electrons.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Electromagnetic Radiation

8.1 In general terms, why do we call light *electromagnetic radiation*?

8.2 In general, what does the term *frequency* imply? What is meant by the term *frequency of light*? What symbol is used for it, and what is the SI unit (and symbol) for frequency?

8.3 What is meant by the term *wavelength* of light? What symbol is used for it?

8.4 Sketch a picture of a wave and label its wavelength and its amplitude.

8.5 Which property of light waves is a measure of the brightness of the light? Which specifies the color of the light? Which is related to the energy of the light?

8.6 Arrange the following regions of the electromagnetic spectrum in order of increasing wavelength (i.e., shortest wavelength $\longrightarrow$ longest wavelength): microwave, TV, X rays, ultraviolet, visible, infrared, gamma rays.

8.7 What wavelength range is covered by the *visible spectrum*?

8.8 Arrange the following colors of visible light in order of increasing wavelength: orange, green, blue, yellow, violet, red.

8.9 Write the equation that relates the wavelength and frequency of a light wave. (Define all symbols used.)

8.10 How is the frequency of a particular type of radiation related to the energy associated with it? (Give an equation, defining all symbols.)

8.11 What is a photon?

8.12 Show that the energy of a photon is given by the equation $E = hc/\lambda$.

8.13 Examine each of the following pairs and state which of the two has the higher energy:

(a) microwaves and infrared

(b) visible light and infrared

(c) ultraviolet light and X rays

(d) visible light and ultraviolet light

8.14 What is a quantum of energy?

Atomic Spectra

8.15 What is an atomic spectrum? How does it differ from a continuous spectrum?

8.16 What fundamental fact is implied by the existence of atomic spectra?

Bohr Atom and the Hydrogen Spectrum

8.17 Describe Niels Bohr's model of the structure of the hydrogen atom.

8.18 In qualitative terms, how did Bohr's model account for the atomic spectrum of hydrogen?

8.19 What is the "ground state"?

8.20 In what way was Bohr's theory a success? How was it a failure?

Wave Nature of Matter

8.21 How does the behavior of very small particles differ from that of the larger, more massive objects that we encounter in everyday life? Why don't we notice this same behavior for the larger, more massive objects?

8.22 Describe the phenomenon called diffraction. How can this be used to demonstrate that de Broglie's theory was correct?

8.23 What experiment could you perform to determine whether a beam was behaving as a wave or as a stream of particles?

8.24 What is wave/particle duality?

8.25 What is the difference between a traveling wave and a standing wave?

8.26 What is the collapsing atom paradox?

8.27 How does quantum mechanics resolve the collapsing atom paradox?

Electron Waves in Atoms

8.28 What are the names used to refer to the theories that apply the matter–wave concept to electrons in atoms?

8.29 What is the term used to describe a particular waveform of a standing wave for an electron?

8.30 What are the three properties of orbitals in which we are most interested? Why?

Quantum Numbers

8.31 What are the allowed values of the principal quantum number?

8.32 Why is **(a)** the *d* subshell in the Period 4 designated as 3*d* and **(b)** the *f* subshell in Period 7 designated as 5*f*?

8.33 Why does every shell contain an *s* subshell?

8.34 How many orbitals are found in **(a)** an *s* subshell, **(b)** a *p* subshell, **(c)** a *d* subshell, and **(d)** an *f* subshell?

8.35 If the value of m_ℓ for an electron in an atom is 2, could another electron in the same subshell have $m_\ell = -3$?

8.36 Suppose an electron in an atom has the following set of quantum numbers: $n = 2$, $\ell = 1$, $m_\ell = 1$, $m_s = +\frac{1}{2}$. What set of quantum numbers is impossible for another electron in this same atom?

Electron Spin

8.37 What physical property of electrons leads us to propose that they spin like a toy top?

8.38 What is the name of the magnetic property exhibited by atoms that contain unpaired electrons?

8.39 What is the Pauli exclusion principle? What effect does it have on the populating of orbitals by electrons?

8.40 What are the possible values of the spin quantum number?

Electron Configuration of Atoms

8.41 What do we mean by the term *electronic structure?*

8.42 Within any given shell, how do the energies of the *s*, *p*, *d*, and *f* subshells compare?

8.43 What fact about the energies of subshells was responsible for the apparent success of Bohr's theory about electronic structure?

8.44 How do the energies of the orbitals belonging to a given subshell compare?

8.45 Give the electron configurations of the elements in Period 2 of the periodic table.

8.46 Give the correct electron configurations of **(a)** Cr and **(b)** Cu.

8.47 What is the correct electron configuration of silver?

8.48 How are the electron configurations of the elements in a given group similar? Illustrate your answer by writing shorthand configurations for the elements in Group 6A.

8.49 Define the terms *valence shell* and *valence electrons.*

Shapes of Atomic Orbitals

8.50 Why do we use probabilities when we discuss the position of an electron in the space surrounding the nucleus of an atom?

8.51 Sketch the approximate shape of **(a)** a 1*s* orbital and **(b)** a 2*p* orbital.

8.52 How does the size of a given type of orbital vary with *n*?

8.53 How are the *p* orbitals of a given *p* subshell oriented relative to each other?

8.54 What is a *nodal plane*?

8.55 What is a radial node?

8.56 How many nodal planes does a *p* orbital have? How many does a *d* orbital have?

8.57 On appropriate coordinate axes, sketch the shape of the following *d* orbitals: **(a)** d_{xy}, **(b)** $d_{x^2-y^2}$, **(c)** d_{z^2}.

Atomic and Ionic Size

8.58 What is the meaning of *effective nuclear charge?* How does the effective nuclear charge felt by the outer electrons vary going down a group? How does it change as we go from left to right across a period?

8.59 In what region of the periodic table are the largest atoms found? Where are the smallest atoms found?

8.60 Going from left to right in the periodic table, why are the size changes among the transition elements more gradual than those among the representative elements?

Ionization Energy

8.61 Define ionization energy. Why are ionization energies of atoms and positive ions endothermic quantities?

8.62 For oxygen, write an equation for the change associated with **(a)** its first ionization energy and **(b)** its third ionization energy.

8.63 Explain why ionization energy increases from left to right in a period and decreases from top to bottom in a group.

8.64 Why is an atom's second ionization energy always larger than its first ionization energy?

8.65 Why is the fifth ionization energy of carbon so much larger than its fourth?

8.66 Why is the first ionization energy of aluminum less than the first ionization energy of magnesium?

8.67 Why does phosphorus have a larger first ionization energy than sulfur?

Electron Affinity

8.68 Define *electron affinity*.

8.69 For sulfur, write an equation for the change associated with **(a)** its first electron affinity and **(b)** its second electron affinity. How should they compare?

8.70 Why does Cl have a more exothermic electron affinity than F? Why does Br have a less exothermic electron affinity than Cl?

8.71 Why is the second electron affinity of an atom always endothermic?

8.72 How is electron affinity related to effective nuclear charge? On this basis, explain the relative magnitudes of the electron affinities of oxygen and fluorine.

Review Problems

Electromagnetic Radiation

8.73 What is the frequency in hertz of blue light having a wavelength of 436 nm?

OH **8.74** Ultraviolet light with a wavelength of more than 295 nm has little germicidal value. What is the frequency that corresponds to this wavelength?

8.75 A certain substance strongly absorbs infrared light having a wavelength of 6.85 μm. What is the frequency of this light in hertz?

8.76 The sun emits many wavelengths of light. The brightest light is emitted at about 0.48 μm. What frequency does this correspond to?

8.77 Ozone protects the earth's inhabitants from the harmful effects of ultraviolet light arriving from the sun. This shielding is a maximum for UV light having a wavelength of 295 nm. What is the frequency in hertz of this light?

8.78 The meter is defined as the length of the path light travels in a vacuum during the time interval of 1/299,792,458 of a second. The standards body recommends use of light from a helium–neon laser for defining the meter. The light from the laser has a wavelength of 632.99139822 nm. What is the frequency of this light, in hertz?

8.79 In New York City, radio station WCBS broadcasts its FM signal at a frequency of 101.1 megahertz (MHz). What is the wavelength of this signal in meters?

8.80 Sodium vapor lamps are often used in residential street lighting. They give off a yellow light having a frequency of 5.09×10^{14} Hz. What is the wavelength of this light in nanometers?

8.81 There has been some concern in recent times about possible hazards to people who live very close to high-voltage electric power lines. The electricity in these wires oscillates at a frequency of 60.0 Hz, which is the frequency of any electromagnetic radiation that they emit. What is the wavelength of this radiation in meters? What is it in kilometers?

8.82 An X-ray beam has a frequency of 1.50×10^{18} Hz. What is the wavelength of this light in nanometers and in picometers?

8.83 Calculate the energy in joules of a photon of red light having a frequency of 4.0×10^{14} Hz. What is the energy of one mole of these photons?

8.84 Calculate the energy in joules of a photon of green light having a wavelength of 563 nm.

Atomic Spectra

8.85 In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. **(a)** What color is this line? **(b)** What is its frequency? **(c)** What is the energy of each of its photons?

8.86 In the spectrum of sodium, there is a line with a wavelength of 589 nm. **(a)** What color is this line? **(b)** What is its frequency? **(c)** What is the energy of each of its photons?

OH 8.87 Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which $n_2 = 6$ and $n_1 = 3$. (Report your answer using three significant figures.) Would we be expected to see the light corresponding to this spectral line? Explain your answer.

8.88 Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which $n_2 = 5$ and $n_1 = 2$. (Report your answer using three significant figures.) Would we be expected to see the light corresponding to this spectral line? Explain your answer.

8.89 Calculate the wavelength of the spectral line produced in the hydrogen spectrum when an electron falls from the tenth Bohr orbit to the fourth. (Report your answer using three significant figures.) In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?

***8.90** Calculate the energy in joules and the wavelength in nanometers of the spectral line produced in the hydrogen spectrum when an electron falls from the fourth Bohr orbit to the first. (Report your answer using three significant figures.) In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?

Quantum Numbers

8.91 What is the letter code for a subshell with **(a)** $\ell = 1$ and **(b)** $\ell = 3$?

8.92 What is the value of ℓ for **(a)** an *f* orbital and **(b)** a *d* orbital?

8.93 What are the values of n and ℓ for the following subshells: **(a)** $3s$, **(b)** $5d$?

8.94 Give the values of n and ℓ for the following subshells: **(a)** $4p$, **(b)** $6f$.

8.95 For the shell with $n = 6$, what are the possible values of ℓ

8.96 In a particular shell, the largest value of ℓ is 7. What is the value of n for this shell?

8.97 What are the possible values of m_ℓ for a subshell with **(a)** $\ell = 1$ and **(b)** $\ell = 3$?

8.98 If the value of ℓ for an electron in an atom is 5, what are the possible values of m_ℓ that this electron could have?

8.99 If the value of m_ℓ for an electron in an atom is -4, what is the smallest value of ℓ that the electron could have? What is the smallest value of n that the electron could have?

8.100 How many orbitals are there in an h subshell ($\ell = 5$)? What are their values of m_ℓ?

OH 8.101 Give the complete set of quantum numbers for all of the electrons that could populate the $2p$ subshell of an atom.

8.102 Give the complete set of quantum numbers for all of the electrons that could populate the $3d$ subshell of an atom.

***8.103** In an antimony atom, how many electrons have $\ell = 1$? How many electrons have $\ell = 2$ in an antimony atom?

***8.104** In an atom of barium, how many electrons have **(a)** $\ell = 0$ and **(b)** $m_\ell = 1$?

Electron Configuration of Atoms

8.105 Give the electron configurations of **(a)** S, **(b)** K, **(c)** Ti, and **(d)** Sn.

8.106 Write the electron configurations of **(a)** As, **(b)** Cl, **(c)** Ni, and **(d)** Si.

8.107 Which of the following atoms in their ground states are expected to be paramagnetic: **(a)** Mn, **(b)** As, **(c)** S, **(d)** Sr, **(e)** Ar?

8.108 Which of the following atoms in their ground states are expected to be diamagnetic: **(a)** Ba, **(b)** Se, **(c)** Zn, **(d)** Si?

OH ILW 8.109 How many unpaired electrons would be found in the ground state of **(a)** Mg, **(b)** P, and **(c)** V?

8.110 How many unpaired electrons would be found in the ground state of **(a)** Cs, **(b)** S, and **(c)** Ni?

8.111 Write the shorthand electron configurations for **(a)** Ni, **(b)** Cs, **(c)** Ge, **(d)** Br, and **(e)** Bi.

8.112 Write the shorthand electron configurations for **(a)** Al, **(b)** Se, **(c)** Ba, **(d)** Sb, and **(e)** Gd.

8.113 Draw complete orbital diagrams for **(a)** Mg and **(b)** Ti.

8.114 Draw complete orbital diagrams for **(a)** As and **(b)** Ni.

8.115 Draw orbital diagrams for the shorthand configurations of **(a)** Ni, **(b)** Cs, **(c)** Ge, and **(d)** Br.

8.116 Draw orbital diagrams for the shorthand configurations of **(a)** Al, **(b)** Se, **(c)** Ba, and **(d)** Sb.

8.117 What is the value of n for the valence shells of **(a)** Sn, **(b)** K, **(c)** Br, and **(d)** Bi?

8.118 What is the value of n for the valence shells of **(a)** Al, **(b)** Se, **(c)** Ba, and **(d)** Sb?

8.119 Give the configuration of the valence shell for **(a)** Na, **(b)** Al, **(c)** Ge, and **(d)** P.

8.120 Give the configuration of the valence shell for **(a)** Mg, **(b)** Br, **(c)** Ga, and **(d)** Pb.

8.121 Draw the orbital diagram for the valence shell of **(a)** Na, **(b)** Al, **(c)** Ge, and **(d)** P.

8.122 Draw the orbital diagram for the valence shell of **(a)** Mg, **(b)** Br, **(c)** Ga, and **(d)** Pb.

Atomic Properties

8.123 If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in **(a)** Na, **(b)** S, **(c)** Cl?

8.124 If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in **(a)** Mg, **(b)** Si, **(c)** Br?

8.125 Choose the larger atom in each pair: **(a)** Mg or S; **(b)** As or Bi.

8.126 Choose the larger atom in each pair: **(a)** Al or Ar; **(b)** Tl or In.

8.127 Choose the largest atom among the following: Ge, As, Sn, Sb.

8.128 Place the following in order of increasing size: N^{3-}, Mg^{2+}, Na^+, Ne, F^-, O^{2-}.

8.129 Choose the larger particle in each pair: **(a)** Na or Na^+; **(b)** Co^{3+} or Co^{2+}; **(c)** Cl or Cl^-.

OH **8.130** Choose the larger particle in each pair: **(a)** S or S^{2-}; **(b)** Al^{3+} or Al; **(c)** Au^+ or Au^{3+}.

8.131 Choose the atom with the larger ionization energy in each pair: **(a)** B or N; **(b)** Se or S; **(c)** Cl or Ge.

8.132 Choose the atom with the larger ionization energy in each pair: **(a)** Li or Rb; **(b)** Al or F; **(c)** F or C.

8.133 Choose the atom with the more exothermic electron affinity in each pair: **(a)** I or Br; **(b)** Ga or As.

8.134 Choose the atom with the more exothermic electron affinity in each pair: **(a)** S or As; **(b)** Si or N.

8.135 Use the periodic table to select the element in the following list for which there is the largest difference between the second and third ionization energies: Na, Mg, Al, Si, P, Se, Cl.

8.136 Use the periodic table to select the element in the following list for which there is the largest difference between the fourth and fifth ionization energies: Na, Mg, Al, Si, P, Se, Cl.

Additional Exercises

8.137 The human ear is sensitive to sound ranging from 20.0 to 2.00×10^4 Hz. The speed of sound is 330 m/s in air, and 1500 m/s under water. What is the longest and the shortest wavelength that can be heard **(a)** in air and **(b)** under water?

*8.138 Microwaves are used to heat food in microwave ovens. The microwave radiation is absorbed by moisture in the food. This heats the water, and as the water becomes hot, so does the food. How many photons having a wavelength of 3.00 mm would have to be absorbed by 1.00 g of water to raise its temperature by 1.00 °C?

8.139 In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. Use the Rydberg equation to calculate the value of *n* for the higher energy Bohr orbit involved in the emission of this light. Assume the value of *n* for the lower energy orbit equals 2.

8.140 Calculate the wavelength in nanometers of the shortest wavelength of light emitted by a hydrogen atom.

8.141 Which of the following electronic transitions could lead to the emission of light from an atom?

$$1s \longrightarrow 4p \longrightarrow 3d \longrightarrow 5f \longrightarrow 4d \longrightarrow 2p$$

8.142 Calculate the wavelengths of the lines in the spectrum of hydrogen that result when an electron falls from a Bohr orbit with **(a)** $n = 5$ to $n = 1$, **(b)** $n = 4$ to $n = 2$, and **(c)** $n = 6$ to $n = 4$. (Report your answer using four significant figures.) In which regions of the electromagnetic spectrum are these lines?

OH **8.143** What, if anything, is wrong with the following electron configurations for atoms in their ground states?

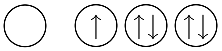
(a) $1s^2 2s^1 2p^3$

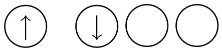
(b) $[Kr]3d^7 4s^2$

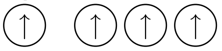
(c) $1s^2 2s^2 2p^4$

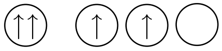
(d) $[Xe]\ 4f^{14} 5d^8 6s^1$

*8.144 Suppose students gave the following orbital diagrams for the 2*s* and 2*p* subshell in the ground state of an atom. What, if anything, is wrong with them? Are any of these electron distributions impossible?

(a)


(b)


(c)


(d)


8.145 How many electrons are in *p* orbitals in an atom of germanium?

8.146 What are the quantum numbers of the electrons that are lost by an atom of iron when it forms the ion Fe^{2+}?

*8.147 The removal of an electron from the hydrogen atom corresponds to raising the electron to the Bohr orbit that has $n = \infty$. On the basis of this statement, calculate the ionization energy of hydrogen in units of **(a)** joules per atom and **(b)** kilojoules per mole.

8.148 Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. On the basis of what you have learned about electron affinities and electron configurations, why is it extremely difficult to place a third electron on the oxygen atom?

*8.149 From the data available in this chapter, determine the ionization energy of **(a)** F^-, **(b)** O^-, and **(c)** O^{2-}. Are any of these energies exothermic?

8.150 For an oxygen atom, which requires more energy, the addition of two electrons or the removal of one electron?

Multi-Concept Problems

***8.151** A neon sign is a gas discharge tube in which electrons traveling from the cathode to the anode collide with neon atoms in the tube and knock electrons off of them. As electrons return to the neon ions and drop to lower energy levels, light is given off. How fast would an electron have to be moving to eject an electron from an atom of neon, which has a first ionization energy equal to 2080 kJ mol^{-1}?

***8.152** OH How many grams of water could have its temperature raised by 5.0 °C by a mole of photons that have a wavelength of **(a)** 600 nm and **(b)** 300 nm?

***8.153** OH It has been found that when the chemical bond between chlorine atoms in Cl_2 is formed, 328 kJ is released per mole of Cl_2 formed. What is the wavelength of light that would be required to break chemical bonds between chlorine atoms?

***8.154** Using the ionization energy for sodium, would a photon with a wavelength of 23.7 nm be able to transfer enough energy to an electron in a sodium atom to cause it to ionize if all of the energy of the photon is transferred to the $3s^1$ electron of sodium? What is the maximum kinetic energy of the ejected electron?

***8.155** Using photons with a wavelength of 23.7 nm, determine the kinetic energies of all of the electrons that can be observed from a sample of boron.

Exercises in Critical Thinking

8.156 Our understanding of the quantum mechanical atom has been developing since the early 1900s. Has quantum mechanics had any effect on the daily lives of people?

8.157 When a copper atom loses an electron to become a Cu^+ ion, what are the possible quantum numbers of the electron that was lost?

8.158 Paired electrons cancel each other's magnetic fields. Why can't unpaired electrons have opposite spins and cancel each other's magnetic fields also?

8.159 Placing a small piece of an element from Group 1A in water results in increasingly rapid and violently spectacular reactions as we progress from lithium down to cesium. What information in this chapter makes this behavior understandable?

9 The Basics of Chemical Bonding

Chapter Outline

9.1 | Energy Requirements for Bond Formation

9.2 | Ionic Bonding

9.3 | Electron Configurations of Ions

9.4 | Lewis Symbols: Keeping Track of Valence Electrons

9.5 | Covalent Bonds

9.6 | Covalent Compounds of Carbon

9.7 | Bond Polarity and Electronegativity

9.8 | Lewis Structures

9.9 | Resonance Structures

This mountain climber's fate hangs on the strength of the chemical bonds between the atoms forming the fibers in the rope keeping her from falling to her death. Chemical bonds affect the chemical and physical properties of substances, both of which are important criteria when selecting materials for practical uses. In this chapter we begin our study of the way atoms bond to each other. | Love Images/© Corbis

This Chapter in Context

In Chapter 3 you learned that we can classify substances into two broad categories, ionic or molecular. Ionic compounds, such as ordinary table salt, consist of electrically charged particles (ions) that bind to each other by electrostatic forces of attraction. We also said that in molecular substances, such as water, the atoms are held to each other by the sharing of electrons. Now that you've learned about the electronic structures of atoms, we can explore the attractions between atoms or ions, called **chemical bonds,** in greater depth. Our goal is to gain some insight into the reasons certain combinations of atoms prefer electron transfer and the formation of ions (leading to *ionic bonding*), while other combinations bind by electron sharing (leading to *covalent bonding*).

As with electronic structure, models of chemical bonding have also evolved, and in this chapter we introduce you to relatively simple theories. Although more complex theories exist (some of which we describe in Chapter 10), the basic concepts you will study in this chapter still find many useful applications in modern chemical thought.

9.1 | Energy Requirements for Bond Formation

■ The heat of reaction is just one factor that determines whether or not a chemical reaction can occur spontaneously. We will discuss this in detail in Chapter 19.

For a *stable* compound to be formed from its elements, the reaction must be exothermic. In other words, ΔH_f° must be negative. Two examples of such reactions are the formation of H_2O by the reaction of H_2 with O_2 (Figure 1.22, page 20) and the formation of NaCl by the reaction of Na with Cl_2, shown in Figure 9.1. Both of these reactions release a large amount of energy when they occur and produce very stable compounds. Typically, compounds with positive heats of formation tend to be unstable with respect to decomposition. Sometimes that decomposition can occur violently, as with nitroglycerine, a powerful explosive.

When a reaction is exothermic, the potential energy of the particles in the system decreases. Therefore, to understand the formation of chemical bonds, we need to understand how bond formation can lead to a lowering of the potential energy of the atoms involved. In the pages ahead we will examine this for both ionic and molecular substances.

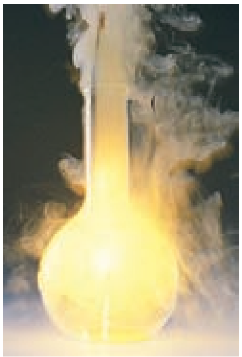


Figure 9.1 | **Exothermic reaction of sodium with chlorine.** A small piece of melted sodium immediately ignites when dipped into a flask containing chlorine gas, producing light and releasing a lot of heat. The smoke coming from the flask is composed of fine crystals of sodium chloride. *(Richard Megna/Fundamental Photographs)*

9.2 | Ionic Bonding

You learned in Chapter 3 that when sodium chloride is formed from its elements, each sodium atom loses one electron to form a sodium ion, Na^+, and each chlorine atom gains one electron to become a chloride ion, Cl^-.

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$$
$$\mathrm{Cl} + e^- \longrightarrow \mathrm{Cl}^-$$

Once formed, these ions become tightly packed together, as illustrated in Figure 9.2, because their opposite charges attract. *This attraction between positive and negative ions in an ionic compound is what we call an* **ionic bond**.

The attraction between Na^+ and Cl^- ions may seem reasonable, but *why* are electrons transferred between these and other atoms? *Why* does sodium form Na^+ and not Na^- or Na^{2+}? And *why* does chlorine form Cl^- instead of Cl^+ or Cl^{2-}? To answer such questions we have to consider factors that are related to the potential energy of the system of reactants and products. As noted above, for any stable compound to form from its elements, there must be a net lowering of the potential energy and the reaction must be exothermic.

■ Keep in mind the relationship between potential energy changes and endothermic and exothermic processes:

endothermic ⇔ increase in PE
exothermic ⇔ decrease in PE

Importance of the Lattice Energy

In the formation of an ionic compound such as NaCl, it is not the electron transfer itself that leads to a stable substance. We can see this if we examine the ionization energy of Na and the electron affinity of Cl. Dealing with a mole-sized collection of gaseous atoms, we have

$$\begin{array}{rlrl} \mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + e^- & & +495.4\ \mathrm{kJ\ mol^{-1}} & \text{(IE of sodium)} \\ \mathrm{Cl}(g) + e^- \longrightarrow \mathrm{Cl}^-(g) & & -348.8\ \mathrm{kJ\ mol^{-1}} & \text{(EA of chlorine)} \\ \hline & \text{Net} & +146.6\ \mathrm{kJ\ mol^{-1}} & \end{array}$$

Notice that forming gaseous sodium and chloride ions from gaseous sodium and chlorine atoms requires a substantial *increase* in the potential energy. This tells us that if the IE and EA were the only energy changes involved, ionic sodium chloride would not form from atoms of sodium and chlorine. So where does the stability of the compound come from?

In the calculation above, we looked at the formation of gaseous ions, but salt is not a gas; it's a solid. Therefore, we need to see how the energy would change if the gaseous ions are condensed to give the solid, and to do this we must examine a quantity called the lattice energy.

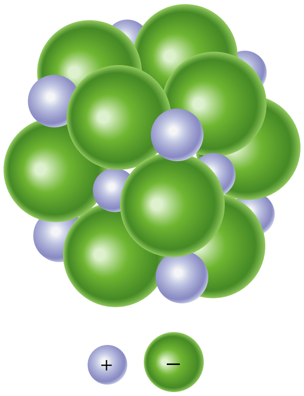


Figure 9.2 | **The packing of ions in NaCl.** Electrostatic forces hold the ions in place in the solid. These forces constitute ionic bonds.

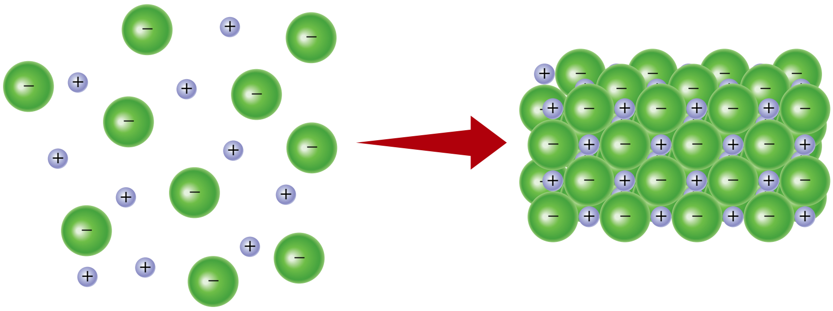
The **lattice energy** *is the energy change that would occur if the ions at infinite separation (i.e., a cloud of gaseous ions) are brought together to form one mole of the solid compound.*[1] For sodium chloride, the change associated with the lattice energy is pictured in Figure 9.3, and in equation form can be represented as

■ The name lattice energy comes from the word *lattice*, which is used to describe the regular pattern of ions or atoms in a crystal. Lattice energies are exothermic and so are given negative signs.

$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s)$$

Because Na^+ and Cl^- ions attract each other, their potential energy decreases as they come together, so the process releases energy and is exothermic. In fact, the lattice energy for sodium chloride is very exothermic and is equal to $-787\ \mathrm{kJ\ mol^{-1}}$. If we include the lattice energy along with the ionization energy of Na and electron affinity of Cl, we have

$$\begin{array}{rlrl} \mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + e^- & & +495.4\ \mathrm{kJ} & \text{(IE of sodium)} \\ \mathrm{Cl}(g) + e^- \longrightarrow \mathrm{Cl}^-(g) & & -348.8\ \mathrm{kJ} & \text{(EA of chlorine)} \\ \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s) & & -787.0\ \mathrm{kJ} & \text{(lattice energy)} \\ \hline & \text{Net} & -640.4\ \mathrm{kJ} & \end{array}$$



1 mol Na^+ and 1 mol Cl^-
(gaseous ions from NaCl)

1 mol NaCl
(solid, crystalline NaCl)

Figure 9.3 | **The lattice energy of NaCl.** The energy released when one mole of gaseous Na^+ and one mole of gaseous Cl^- condenses to one mole of solid NaCl is the lattice energy. For NaCl, this amounts to 787 kJ.

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[1] In some books, the lattice energy is defined as *the energy needed to separate the ions in one mole of a solid to give a cloud of gaseous ions*. This would correspond to the change

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g)$$

The *magnitude* of the energy change is the same as for the process described above in the body of the text, but the algebraic sign of the energy change would be positive instead of negative (endothermic instead of exothermic).

Thus, the release of energy equal to the lattice energy provides a large net lowering of the potential energy as solid NaCl is formed. We can also say that *it is the lattice energy that provides the stabilization necessary for the formation of NaCl.* Without it, the compound could not exist.

Determining Lattice Energies

At this point, you may be wondering about our starting point in these energy calculations—namely, gaseous sodium atoms and chlorine atoms. In nature, sodium is a solid metal and chlorine consists of gaseous Cl_2 molecules. Let's look at a complete analysis of the energy changes taking this into account. To perform the analysis we will use an enthalpy diagram similar to the type discussed in Chapter 7. It is called a **Born–Haber cycle** after the scientists who were the first to use it to calculate lattice energies.

In Chapter 7 you learned that the enthalpy change for a process is the same regardless of the path we follow from start to finish. With this in mind, we will construct two different paths from the free elements (solid sodium and gaseous chlorine molecules) to the solid ionic compound, sodium chloride, as shown in Figure 9.4.

The starting point for both paths is the same: the free elements sodium and chlorine. The path that starts at the lower left takes us directly to the product, NaCl(*s*), and has as its enthalpy change the heat of formation of NaCl, ΔH°_f.

$$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H^\circ_f = -411.3 \text{ kJ}$$

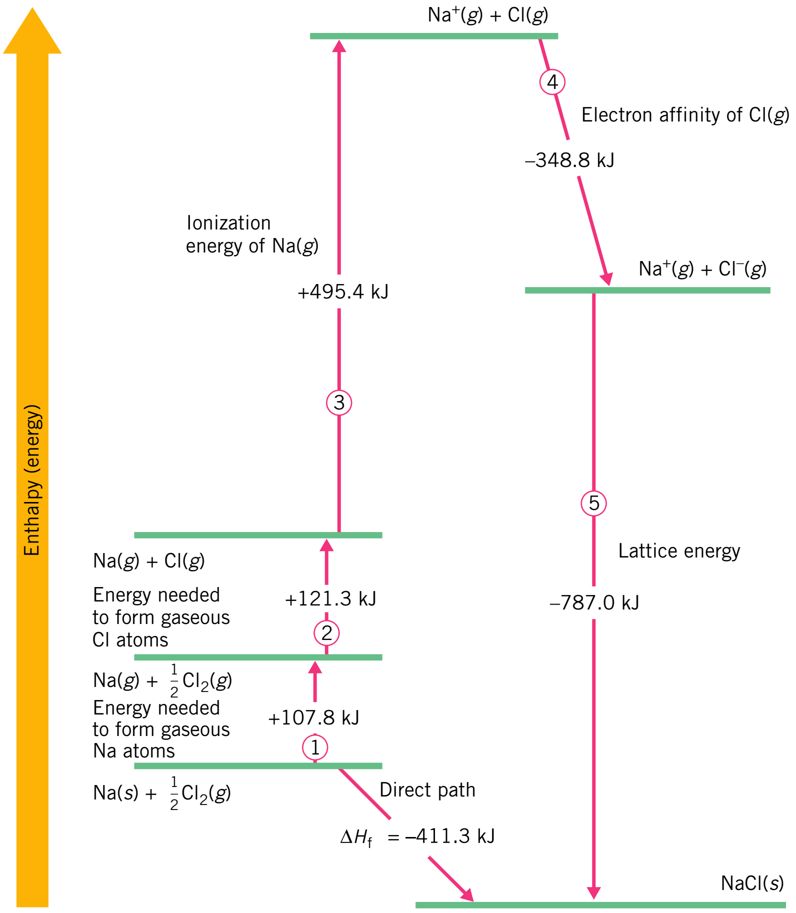
Enthalpy (energy)
Na+(g) + Cl(g)
4
Electron affinity of Cl(g)
–348.8 kJ
Na+(g) + Cl−(g)
Ionization energy of Na(g)
+495.4 kJ
3
5
Lattice energy
–787.0 kJ
Na(g) + Cl(g)
Energy needed to form gaseous Cl atoms
+121.3 kJ
2
Na(g) + 1/2 Cl2(g)
Energy needed to form gaseous Na atoms
+107.8 kJ
1
Na(s) + 1/2 Cl2(g)
Direct path
ΔHf = –411.3 kJ
NaCl(s)

Figure 9.4 | **Analysis of the enthalpy changes in the formation of sodium chloride.** One path leads directly from the elements Na(*s*) and $Cl_2(g)$ to NaCl(*s*). The second (upper) path follows a series of changes that include the lattice energy and take us to the same final product, NaCl(*s*).

The alternative path is divided into a number of steps. The first two, labeled 1 and 2, have $\Delta H°$ values that can be measured experimentally and both are endothermic. They change Na(s) and $Cl_2(g)$ into gaseous atoms, Na(g) and Cl(g). The next two steps (Steps 3 and 4) change the atoms to ions, first by the endothermic ionization energy (IE) of Na followed by the exothermic electron affinity (EA) of Cl. This brings us to the gaseous ions, $Na^+(g) + Cl^-(g)$, depicted on the right in Figure 9.4. Notice that at this point, if we add all the energy changes, the ions are at a considerably higher energy than the reactants. If these were the only energy terms involved in the formation of NaCl, the heat of formation would be endothermic and the compound would be unstable; it could not be formed by the direct combination of the elements.

The last step on the right in Figure 9.4 (Step 5) finally brings us to solid NaCl and corresponds to the lattice energy. To make the net energy changes the same along both paths, the energy released when the ions condense to form the solid must equal −787.0 kJ. Therefore, the calculated lattice energy of NaCl must be $-787.0 \text{ kJ mol}^{-1}$.

What we see in this analysis is that it is the lattice energy that permits NaCl to be formed from its elements. In fact, *for any ionic compound, the chief stabilizing influence is the lattice energy, which when released is large enough to overcome the net energy input required to form the ions from the elements.*

Besides affecting the ability of ionic compounds to form, lattice energies are also important in determining the solubilities of ionic compounds in water and other solvents. We will explore this topic in Chapter 14.

Effect of Ionic Size and Charge on the Lattice Energy

The lattice energies of some ionic compounds are given in Table 9.1. As you can see, they are all very large exothermic quantities. Their magnitudes depend on a number of factors, including the charges on the ions and their sizes.

For two ions with charges q_1 and q_2 separated by a distance r, the potential energy can be calculated from **Coulomb's law:**

$$E = \frac{q_1 q_2}{k r} \tag{9.1}$$

where k is a proportionality constant.[2] In an ionic solid, q_1 and q_2 have opposite signs, so E is calculated to be a negative quantity. That's why the lattice energy has a negative sign.

When the charges on the ions become larger (i.e., when q_1 and q_2 become larger), E becomes more negative, which means the potential energy becomes lower (more negative).

Table 9.1 Lattice Energies of Some Ionic Compounds

Compound	Ions	Lattice Energy (kJ mol^{-1})
LiCl	Li^+ and Cl^-	−845
NaCl	Na^+ and Cl^-	−787
KCl	K^+ and Cl^-	−709
LiF	Li^+ and F^-	−1033
$CaCl_2$	Ca^{2+} and Cl^-	−2258
$AlCl_3$	Al^{3+} and Cl^-	−5492
CaO	Ca^{2+} and O^{2-}	−3401
Al_2O_3	Al^{3+} and O^{2-}	−15,916

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[2] In this case, we're using the symbol q to mean electric charge, not heat as in Chapter 7. Because the number of letters in the alphabet is limited, it's not uncommon in science for the same letter to be used to stand for different quantities. This usually doesn't present a problem as long as the symbol is defined in the context in which it is used.

This explains why salts of Ca^{2+} have larger lattice energies than comparable salts of Na^+, and those containing Al^{3+} have even larger lattice energies.

Because the distance between the ions, r, appears in the denominator in Equation 9.1, E becomes a larger negative quantity as r becomes smaller. As a result, compounds formed from small ions (which can get close together) have larger lattice energies than those formed from large ions. For example, a Na^+ ion is smaller than a K^+ ion, and in Figure 9.5 we compare the cation–anion distances observed in solid NaCl and KCl. The smaller Na–Cl distance causes NaCl to have a larger lattice energy than KCl.

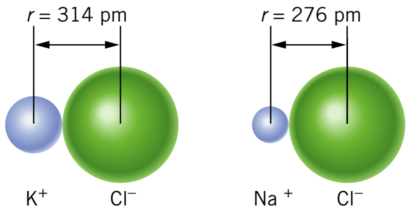


Figure 9.5 | **The effect of ionic size on the lattice energy.** Because Na^+ is smaller than K^+, the distance between ions is smaller in NaCl than in KCl. This causes the lattice energy of NaCl to be larger than that of KCl.

Factors That Determine the Formation of Cations and Anions

We've shown that for an ionic compound to form, the energy lowering produced by release of the lattice energy must exceed the energy rise associated with forming the ions from the neutral atoms. This requires that the cation be formed from an atom of relatively low ionization energy; such atoms are found among the metals. Nonmetals, at the upper right of the periodic table, have large ionization energies but generally exothermic electron affinities. A nonmetal atom has little tendency to lose electrons, but forming an anion from a nonmetal atom can actually help to lower the energy. As a result, cations are formed from metals and anions are formed from nonmetals because this leads to the greatest lowering of the energy. In fact, metals combine with nonmetals to form ionic compounds simply because ionic bonding is favored energetically over other types whenever atoms with small ionization energies combine with atoms that have large exothermic electron affinities.

9.3 | Electron Configurations of Ions

Stability of the Noble Gas Configuration

Earlier we raised the question about why sodium forms Na^+ and chlorine forms Cl^-. To find the answer, let's begin by examining what happens when a sodium atom loses an electron. The electron configuration of Na is

$$\text{Na} \qquad 1s^2 2s^2 2p^6 3s^1$$

The electron that is lost is the one least tightly held, which is the single outer $3s$ electron. The electronic structure of the Na^+ ion, then, is

$$\text{Na}^+ \qquad 1s^2 2s^2 2p^6$$

Notice that this is identical to the electron configuration of the noble gas neon. We say the Na^+ ion has achieved a *noble gas configuration*.

The energy needed to remove the first electron from Na is relatively small and can easily be recovered by the release of the lattice energy when an ionic compound containing Na^+ is formed. However, removal of a second electron from sodium is *very* difficult because it involves breaking into the $2s^2 2p^6$ core. Forming the Na^{2+} ion is therefore very endothermic, as we can see by adding the first and second ionization energies (Table 8.2, page 343).

$$\begin{array}{lll}
\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^- & \text{1st IE} = & 496 \text{ kJ mol}^{-1} \\
\text{Na}^+(g) \longrightarrow \text{Na}^{2+}(g) + e^- & \text{2nd IE} = & \underline{4563 \text{ kJ mol}^{-1}} \\
 & \text{Total} & 5059 \text{ kJ mol}^{-1}
\end{array}$$

This value is so large because the second electron is removed from the noble gas core beneath the outer shell of sodium.

Even though the Na^{2+} ion would give a compound such as $NaCl_2$ a larger lattice energy than NaCl (e.g., see the lattice energy for $CaCl_2$), it would not be large enough to make the formation of the compound exothermic. As a result, $NaCl_2$ cannot form. The same applies to other compounds of sodium, so when sodium forms a cation, electron loss stops once the Na^+ ion is formed and a noble gas electron configuration is reached.

Similar situations exist for other metals, too. For example, the first two electrons to be removed from a calcium atom come from the 4*s* valence shell (outer shell).

$$\begin{array}{ll} \text{Ca} & 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \\ \text{Ca}^{2+} & 1s^2 2s^2 2p^6 3s^2 3p^6 \end{array}$$

The energy needed to accomplish this can be recovered by the release of the lattice energy when a compound containing Ca^{2+} forms. Electron loss ceases at this point, however, because of the huge amount of energy needed to break into the noble gas core. As a result, a calcium atom loses just two electrons when it reacts.

■ For calcium:

1st IE = 590 kJ/mol
2nd IE = 1146 kJ/mol
3rd IE = 4940 kJ/mol

For sodium and calcium, as well as other metals of Groups 1A and 2A and aluminum, the large ionization energy of the noble gas core just below their outer shells limits the number of electrons they lose, so the ions that are formed have noble gas electron configurations.

Nonmetals also tend to achieve noble gas configurations when they form anions. For example, when a chlorine atom reacts, it gains one electron.

$$\begin{array}{ll} \text{Cl} & 1s^2 2s^2 2p^6 3s^2 3p^5 \\ \text{Cl}^- & 1s^2 2s^2 2p^6 3s^2 3p^6 \end{array}$$

At this point, we have a noble gas configuration (that of argon). Electron gain ceases, because if another electron were to be added, it would have to enter an orbital in the next higher shell, which is very energetically unfavorable. Similar arguments apply to the other nonmetals as well.

The Octet Rule

In the preceding discussion you learned that a balance of energy factors causes many atoms to form ions that have a noble gas electron configuration. Historically, this is expressed in the form of a generalization: *When they form ions, atoms of most of the representative elements tend to gain or lose electrons until they have obtained an electron configuration identical to that of the nearest noble gas.* Because all the noble gases except helium have outer shells with eight electrons, this rule has become known as the **octet rule,** which can be stated as follows: *Atoms tend to gain or lose electrons until they have achieved an outer shell that contains an* **octet of electrons** *(eight electrons).*

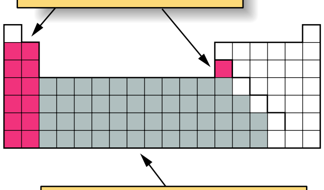
TOOLS

Electron configurations of ions of the representative elements.

Cations That Do Not Obey the Octet Rule

The octet rule, as applied to ionic compounds, really works well only for the cations of the Group 1A and 2A metals and aluminum, and for the anions of the nonmetals. It does not work well for the transition metals and post-transition metals (the metals that follow a row of transition metals).

To obtain the correct electron configurations of the cations of these metals, we apply the following rules:



Octet rule works well for ions of these metals.

Octet rule does not work well for ions of these metals.

> **Obtaining the Electron Configuration of a Cation**
> 1. The first electrons to be lost by an atom or ion are *always* those from the shell with the largest value of *n* (i.e., the outer shell).
> 2. As electrons are removed from a given shell, they come from the highest-energy occupied subshell first, before any are removed from a lower-energy subshell. Within a given shell, the energies of the subshells vary as follows: $s < p < d < f$. This means that *f* is emptied before *d*, which is emptied before *p*, which is emptied before *s*.

TOOLS

Order in which electrons are lost from an atom.

■ Applying these rules to the metals of Groups 1A and 2A also gives the correct electron configurations.

Let's look at two examples.

Tin (a post-transition metal) forms two ions, Sn^{2+} and Sn^{4+}. The electron configurations are

$$\begin{array}{ll} \mathrm{Sn} & [\mathrm{Kr}]\ 4d^{10}5s^{2}5p^{2} \\ \mathrm{Sn}^{2+} & [\mathrm{Kr}]\ 4d^{10}5s^{2} \\ \mathrm{Sn}^{4+} & [\mathrm{Kr}]\ 4d^{10} \end{array}$$

Notice that the Sn^{2+} ion is formed by the loss of the higher energy $5p$ electrons first. Then, further loss of the two $5s$ electrons gives the Sn^{4+} ion. However, neither of these ions has a noble gas configuration.

For the transition elements, the first electrons lost are the s electrons of the outer shell. Then, if additional electrons are lost, they come from the underlying d subshell. An example is iron, which forms the ions Fe^{2+} and Fe^{3+}. The element iron has the electron configuration

$$\mathrm{Fe} \qquad [\mathrm{Ar}]\ 3d^{6}4s^{2}$$

Iron loses its $4s$ electrons fairly easily to give Fe^{2+}, which has the electron configuration

$$\mathrm{Fe} \qquad [\mathrm{Ar}]\ 3d^{6}$$

The Fe^{3+} ion results when another electron is removed, this time from the $3d$ subshell.

$$\mathrm{Fe}^{3+} \qquad [\mathrm{Ar}]\ 3d^{5}$$

Iron is able to form Fe^{3+} because the $3d$ subshell is close in energy to the $4s$, so it is not very difficult to remove the third electron. Notice once again that the first electrons to be removed come from the shell with the largest value of n (the $4s$ subshell). Then, after this shell is emptied, the next electrons are removed from the shell below.

Because so many of the transition elements are able to form ions in a way similar to that of iron, the ability to form more than one positive ion is usually cited as one of the characteristic properties of the transition elements. Frequently, one of the ions formed has a 2+ charge, which arises from the loss of the two outer s electrons. Ions with larger positive charges result when additional d electrons are lost. Unfortunately, it is not easy to predict exactly which ions can form for a given transition metal, nor is it simple to predict their relative stabilities with respect to being oxidized or reduced.

Example 9.1
Writing Electron Configurations of Ions

How do the electron configurations change (a) when a nitrogen atom forms the N^{3-} ion and (b) when an antimony atom forms the Sb^{3+} ion?

■ **Analysis:** For the nonmetals, you've learned that the octet rule does work, so the ion that is formed by nitrogen will have a noble gas configuration.

Antimony is a post-transition element, so we don't expect its cation to obey the octet rule. We will have to examine the electron configuration of the neutral atoms and determine which electrons are lost.

■ **Assembling the Tools:** The octet rule serves as the tool to determine the electron configuration of N^{3-}. To determine the electron configuration of Sb^{3+}, our tools will be the procedure for writing abbreviated electron configurations for atoms as well as the rules describing the order in which electrons are lost from an atom.

■ **Solution:** (a) Following the method for writing abbreviated configurations, the electron configuration for nitrogen is

$$\mathrm{N} \qquad [\mathrm{He}]\ 2s^{2}2p^{3}$$

To form N^{3-}, three electrons are gained. These enter the $2p$ subshell because it is the lowest available energy level. Filling the $2p$ subshell completes the octet; the configuration for the ion is therefore

$$\mathrm{N}^{3-} \qquad [\mathrm{He}]\ 2s^{2}2p^{6}$$

(b) The rules tell us that when a cation is formed, electrons are removed first from the outer shell of the atom (the shell with the largest value of the principal quantum number, *n*). Within a given shell, electrons are always removed first from the subshell highest in energy. Let's begin with the ground state electron configuration for antimony, obtained in the usual way.

$$\text{Sb} \qquad [\text{Kr}]\ 4d^{10}5s^{2}5p^{3}$$

To form the Sb^{3+} ion, three electrons must be removed. These will come from the outer shell, which has $n = 5$. Within this shell, the energies of the subshells increase in the order $s < p < d < f$. Therefore, the 5*p* subshell is higher in energy than the 5*s*, so all three electrons are removed from the 5*p*. This gives

$$\text{Sb}^{3+} \qquad [\text{Kr}]\ 4d^{10}5s^{2}$$

■ Are the Answers Reasonable? In Chapter 3 you learned to use the periodic table to figure out the charges on the anions of the nonmetals. For nitrogen, we would take three steps to the right to get to the nearest noble gas, neon. The electron configuration we obtained for N^{3-} is that of neon, so our answer should be correct.

For antimony, we had to remove three electrons, which completely emptied the 5*p* subshell. That's also good news, because ions do not tend to have partially filled *s* or *p* subshells (although partially filled *d* subshells are not uncommon for the transition metals). If we had taken the electrons from any other subshells, the Sb^{3+} ion would have had a partially filled 5*p* subshell.

Example 9.2
Writing Electron Configurations of Ions

What is the electron configuration of the V^{3+} ion? Give the orbital diagram for the ion.

■ Analysis: To obtain the electron configuration of a cation, always begin with the electron configuration of the neutral atom. In this case we will remove three electrons to obtain the electron configuration of the ion.

■ Assembling the Tools: Once again, our tools will be the method for deriving electron configurations of atoms and the rules that tell us the order in which electrons are lost by an atom. We will also use Hund's rule, which tells us how electrons populate orbitals of a given subshell.

■ Solution: Following the usual method, the electron configuration of vanadium is

$$\text{V} \qquad \underbrace{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}}_{\text{Argon core}}3d^{3}4s^{2}$$

Notice that we've written the configuration showing the outer shell 4*s* electrons farthest to the right. To form the V^{3+} cation, three electrons must be removed from the neutral atom. We have to keep in mind that the electrons are lost first from the occupied shell with highest *n*. Therefore, the first two come from the 4*s* subshell and the third comes from the 3*d*. This means we won't have to take any from the 3*s* or 3*p* subshells, so the argon core will remain intact. Therefore, let's rewrite the electron configuration in abbreviated form.

$$\text{V} \qquad [\text{Ar}]\ 3d^{3}4s^{2}$$

Removing the three electrons gives

$$\text{V}^{3+} \qquad [\text{Ar}]\ 3d^{2}$$

To form the orbital diagram, we show all five orbitals of the 3*d* subshell and then spread out the two electrons with spins unpaired (Hund's rule). This gives

$$V^{3+} \qquad [\mathrm{Ar}]\ \underbrace{\textcircled{\uparrow}\,\textcircled{\uparrow}\,\bigcirc\,\bigcirc\,\bigcirc}_{3d}$$

■ **Is the Answer Reasonable?** First, we check that we've written the correct electron configuration of vanadium, which we have. (A quick count of the electrons gives 23, which is the atomic number of vanadium.) We've also taken electrons away from the atom following the rules, so the electron configuration of the ion seems okay. Finally, we remembered to show all five orbitals of the 3*d* subshell, even though only two of them are occupied.

Practice Exercises

9.1 | What is wrong with the following electron configuration of the In^+ ion? What should the electron configuration be?

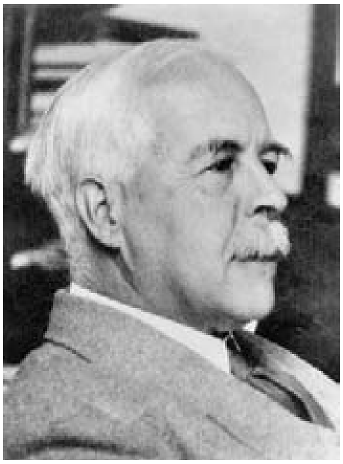
$$In^+ \qquad 1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^15p^1$$

(*Hint:* Check the rules that tell us the order in which electrons are lost by an atom or ion.)

9.2 | How do the electron configurations change when a chromium atom forms the following ions: (a) Cr^{2+}, (b) Cr^{3+}, (c) Cr^{6+}?

9.3 | How are the electron configurations of S^{2-} and Cl^- related?

9.4 | Lewis Symbols: Keeping Track of Valence Electrons



Gilbert N. Lewis, chemistry professor at the University of California, helped develop theories of chemical bonding. In 1916, he proposed that atoms form bonds by sharing pairs of electrons. *(Bettmann/© Corbis)*

TOOLS Lewis symbols

In the previous section you saw how the valence shells of atoms change when electrons are transferred during the formation of ions. We will soon see the way many atoms share their valence electrons with each other when they form covalent bonds. In these discussions it is useful to be able to keep track of valence electrons. To help us do this, we use a simple bookkeeping device called Lewis symbols, named after their inventor, the American chemist, G. N. Lewis (1875–1946).

To draw the **Lewis symbol** for an element, we write its chemical symbol surrounded by dots (or some other similar mark), each of which represents a valence electron of the atom. For example, the element lithium has the Lewis symbol

$$\mathrm{Li}\cdot$$

in which the single dot stands for lithium's single valence electron. In fact, each element in Group 1A has a similar Lewis symbol, because each has only one valence electron. The Lewis symbols for all of the Group 1A metals are

$$\mathrm{Li}\cdot \quad \mathrm{Na}\cdot \quad \mathrm{K}\cdot \quad \mathrm{Rb}\cdot \quad \mathrm{Cs}\cdot$$

The Lewis symbols for the eight A-group elements of Period 2 are[3]

Group	1A	2A	3A	4A	5A	6A	7A	8A
Symbol	$\mathrm{Li}\cdot$	$\cdot\mathrm{Be}\cdot$	$\cdot\dot{\mathrm{B}}\cdot$	$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot$	$\cdot\underset{\cdot}{\dot{\mathrm{N}}}:$	$\cdot\underset{\cdot\cdot}{\dot{\mathrm{O}}}:$	$\cdot\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$	$:\underset{\cdot\cdot}{\ddot{\mathrm{Ne}}}:$

---

[3] For beryllium, boron, and carbon, the number of unpaired electrons in the Lewis symbol doesn't agree with the number predicted from the atom's electron configuration. Boron, for example, has two electrons paired in its 2*s* orbital and a third electron in one of its 2*p* orbitals; therefore, there is actually only one unpaired electron in a boron atom. The Lewis symbols are drawn as shown, however, because when beryllium, boron, and carbon form bonds, they *behave* as if they have two, three, and four unpaired electrons, respectively.

The elements below each of these in their respective groups have identical Lewis symbols except, of course, for the chemical symbol of the element. Notice that when an atom has more than four valence electrons, the additional electrons are shown to be paired with others. Also notice that *for the representative elements, the group number is equal to the number of valence electrons* when the North American convention for numbering groups in the periodic table is followed.

■ This is one of the advantages of the North American convention for numbering groups in the periodic table.

Example 9.3
Writing Lewis Symbols

What is the Lewis symbol for arsenic?

■ **Analysis:** We need to know the number of valence electrons, which we can obtain from the group number. Then we distribute the electrons (dots) around the chemical symbol.

■ **Assembling the Tools:** Our tool is the method described above for constructing the Lewis symbol.

■ **Solution:** The symbol for arsenic is As and we find it in Group 5A. The element therefore has five valence electrons. The first four are placed around the symbol for arsenic as follows:

$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{As}}}\cdot$$

The fifth electron is paired with one of the first four. This gives

$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{As}}}:$$

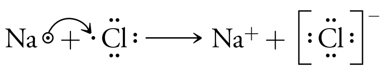
The location of the fifth electron doesn't really matter, so equally valid Lewis symbols are

$$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{As}}}\cdot \quad \text{or} \quad :\overset{\cdot}{\underset{\cdot}{\mathrm{As}}}\cdot \quad \text{or} \quad \cdot\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{As}}}\cdot$$

■ **Is the Answer Reasonable?** There's not much to check here. Have we got the correct chemical symbol? Yes. Do we have the right number of dots? Yes.

Using Lewis Symbols to Represent Ionic Compounds

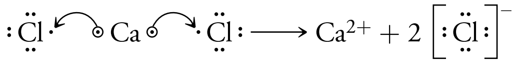
Although we will use Lewis symbols mostly to follow the fate of valence electrons in covalent bonds, they can also be used to describe what happens during the formation of ions. For example, when a sodium atom reacts with a chlorine atom, the sodium loses an electron to the chlorine, which we might depict as



$$\mathrm{Na}\odot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Na}^+ + \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\right]^-$$

The valence shell of the sodium atom is emptied, so no dots remain. The outer shell of chlorine, which formerly had seven electrons, gains one to give a total of eight. The brackets are drawn around the chloride ion to show that all eight electrons are the exclusive property of the Cl^- ion.

We can diagram a similar reaction between calcium and chlorine atoms.



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \;\; \odot\mathrm{Ca}\odot \;\; \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Ca}^{2+} + 2\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\right]^-$$

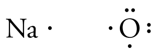
Example 9.4
Using Lewis Symbols

Use Lewis symbols to diagram the reaction that occurs between sodium and oxygen atoms to give Na^+ and O^{2-} ions.

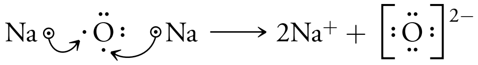
Analysis: For electrical neutrality, the formula will be Na_2O, so we will use two sodium atoms and one oxygen atom. Each sodium will lose one electron to give Na^+ and the oxygen will gain two electrons to give O^{2-}.

Assembling the Tools: The principal tool is the method for constructing the Lewis symbol for an element and its ions.

Solution: Our first task is to draw the Lewis symbols for Na and O.



It takes two electrons to complete the octet around oxygen. Each Na supplies one. Therefore,



Notice that we have put brackets around the oxide ion.

Is the Answer Reasonable? We have accounted for all the valence electrons (an important check), the net charge is the same on both sides of the arrow (the equation is balanced), and we've placed the brackets around the oxide ion to emphasize that the octet belongs exclusively to that ion.

Practice Exercises

9.4 | Use Lewis symbols to diagram the formation of CaI_2 from Ca and I atoms. (*Hint:* Begin by determining how many electrons are gained or lost by each atom.)

9.5 | Diagram the reaction between magnesium and oxygen atoms to give Mg^{2+} and O^{2-} ions.

9.5 | Covalent Bonds

Most of the substances we encounter in our daily lives are not ionic. Instead, they are composed of electrically neutral molecules. The chemical bonds that bind the atoms to each other in such molecules are electrical in nature, but arise from the sharing of electrons rather than by electron transfer.

Energy Changes on Bond Formation

In Section 9.2 we saw that for ionic bonding to occur, the energy-lowering effect of the lattice energy must be greater than the combined net energy-raising effects of the ionization energy (IE) and electron affinity (EA). Many times this is not possible, particularly when the ionization energies of all the atoms involved are large. This happens, for example, when nonmetals combine with each other to form molecules. In such cases, nature uses a different way to lower the energy—electron sharing.

Let's look at what happens when two hydrogen atoms join to form an H_2 molecule (Figure 9.6). As the two atoms approach each other, the electron of each atom begins to feel the attraction of both nuclei. This causes the electron density around each nucleus to shift toward the region between the two atoms. Therefore, as the distance between the nuclei decreases, there is an increase in the probability of finding either electron near either nucleus. In effect, as the molecule is formed, each of the hydrogen atoms in the H_2 molecule acquires a share of two electrons.

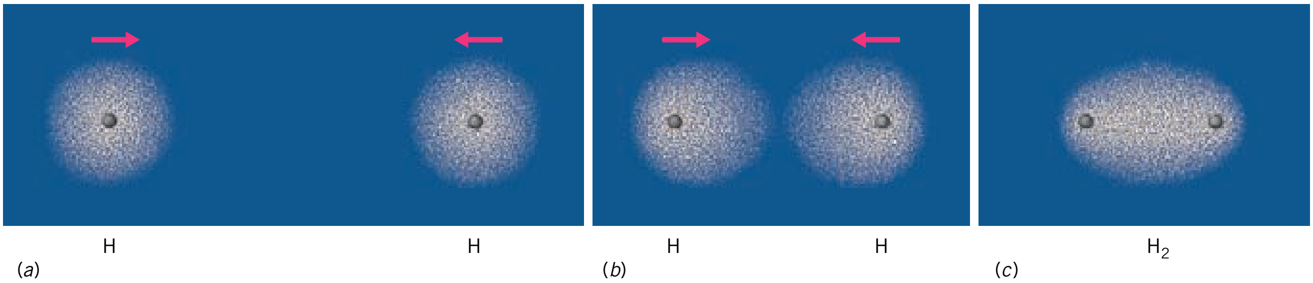


Figure 9.6 | **Formation of a covalent bond between two hydrogen atoms.** (*a*) Two H atoms separated by a large distance. (*b*) As the atoms approach each other, their electron densities are pulled into the region between the two nuclei. (*c*) In the H_2 molecule, the electron density is concentrated between the nuclei. Both electrons in the bond are distributed over both nuclei.

In the H_2 molecule, the buildup of electron density between the two atoms attracts both nuclei and pulls them together. Being of the same charge, however, the two nuclei also repel each other, as do the two electrons. In the molecule that forms, therefore, the atoms are held at a distance at which all these attractions and repulsions are balanced. Overall, the nuclei are kept from separating, and the net force of attraction produced by sharing the pair of electrons is called a **covalent bond.**

Bond Energy and Bond Length

Every covalent bond is characterized by two quantities—namely, the average distance between the nuclei held together by the bond and the amount of energy needed to separate the two atoms to produce neutral atoms again. In the hydrogen molecule, the attractive forces pull the nuclei to a distance of 75 pm, and this distance is called the **bond length** (or sometimes the **bond distance**). Because a covalent bond holds atoms together, work must be done (energy must be supplied) to separate them. The amount of energy needed to "break" the bond (or the energy released when the bond is formed) is called the **bond energy.**

■ As the distance between the nuclei and the electron cloud that lies between them decreases, the potential energy decreases.

Figure 9.7 shows how the potential energy changes when two hydrogen atoms come together to form H_2. We see that the minimum potential energy occurs at a bond length of 75 pm, and that 1 mol of hydrogen molecules is more stable than 2 mol of hydrogen atoms by 435 kJ. In other words, the bond energy of H_2 is 435 kJ/mol.

In general, forming any covalent bond leads to a lowering of the energy and breaking covalent bonds leads to an increase in energy. As noted in Chapter 7, the net energy change we observe in a chemical reaction is the result of energies associated with the breaking and making of bonds.

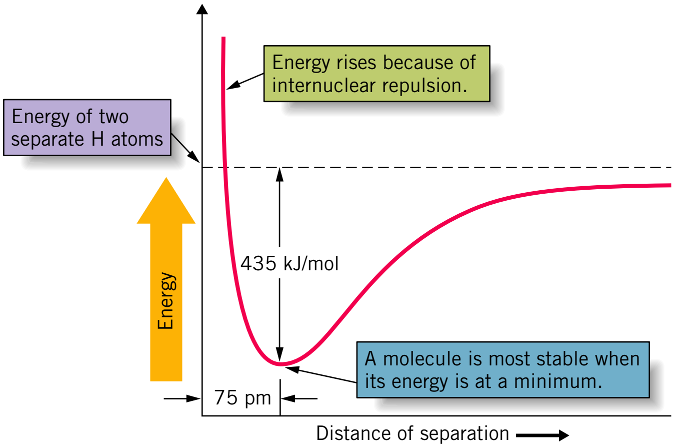


Figure 9.7 | **Changes in the total potential energy of two hydrogen atoms as they form H_2.** The energy of the molecule reaches a minimum when there is a balance between the attractions and repulsions.

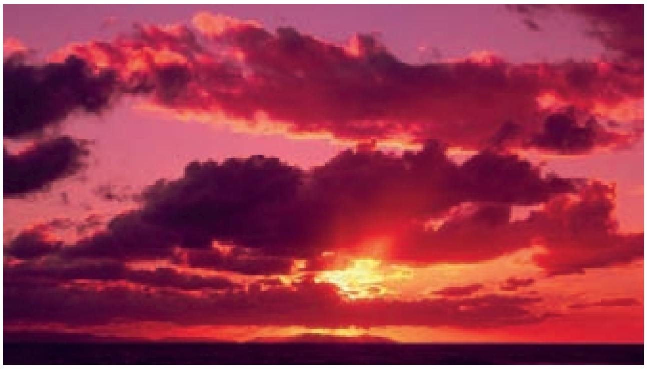
CHEMISTRY AND CURRENT AFFAIRS 9.1

Sunlight and Skin Cancer

The ability of light to provide the energy for chemical reactions enables life to exist on our planet. Green plants absorb sunlight and, with the help of chlorophyll, convert carbon dioxide and water into carbohydrates (e.g., sugars and cellulose), which are essential constituents of the food chain. However, not all effects of sunlight are so beneficial.

As you know, light packs energy that's proportional to its frequency, and if the photons that are absorbed by a substance have enough energy, they can rupture chemical bonds and initiate chemical reactions. Light that is able to do this has frequencies in the ultraviolet (UV) region of the electromagnetic spectrum, and the sunlight bombarding the earth contains substantial amounts of UV radiation. Fortunately, a layer of ozone (O_3) in the stratosphere, a region of the atmosphere extending from about 45 to 55 km altitude, absorbs most of the incoming UV, protecting life on the surface. However, some UV radiation does get through, and the part of the spectrum of most concern is called "UV-B" with wavelengths between 280 and 320 nm.

What makes UV-B so dangerous is its ability to affect the DNA in our cells. (The structure of DNA and its replication is discussed in Chapter 23.) Absorption of UV radiation causes constituents of the DNA, called *pyrimidine bases*, to undergo reactions that form bonds between them. This causes transcription errors when the DNA replicates during cell division, giving rise to genetic mutations that can lead to skin cancers. These skin cancers fall into three classes—basal cell carcinomas, squamous cell carcinomas, and melanomas (the last being the most dangerous). Each year there are more than 1 million cases of skin cancer diagnosed. It is estimated that more than 90% of skin cancers are due to absorption of UV-B radiation.



Dawn of a new day brings the risk of skin cancer to those particularly susceptible. Fortunately, understanding the risk allows us to protect ourselves with clothing and sunblock creams. *© Mick Roessler/© Corbis*

In recent years, concern has grown over the depletion of the ozone layer in the stratosphere apparently caused by the release of gases called chlorofluorocarbons (CFCs), which have been widely used in refrigerators and air conditioners. Some scientists have estimated a substantial increase in the rate of skin cancer caused by increased amounts of UV-B reaching the earth's surface due to this ozone depletion.

Pairing of Electrons in Covalent Bonds

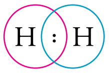
Before joining to form H_2, each of the separate hydrogen atoms has one electron in a 1*s* orbital. When these electrons are shared, the 1*s* orbital of each atom is, in a sense, filled. Because the electrons now share the same space, they become paired as required by the Pauli exclusion principle; that is, m_s is $+\frac{1}{2}$ for one of the electrons and $-\frac{1}{2}$ for the other. In general, the electrons involved almost always become paired when atoms form covalent bonds. In fact, a covalent bond is sometimes referred to as an **electron pair bond**.

■ In Chapter 8 you learned that when two electrons occupy the same orbital and therefore share the same space, their spins must be paired. The pairing of electrons is an important part of the formation of a covalent bond.

Lewis symbols are often used to keep track of electrons in covalent bonds. The electrons that are shared between two atoms are shown as a pair of dots placed between the symbols for the bonded atoms. The formation of H_2 from hydrogen atoms, for example, can be depicted as

$$\mathrm{H}\cdot + \mathrm{H}\cdot \longrightarrow \mathrm{H}:\mathrm{H}$$

Because the electrons are shared, each H atom is considered to have two electrons.



(Colored circles emphasize that two electrons can be counted around each of the H atoms.)

For simplicity, the electron pair in a covalent bond is usually depicted as a single dash. Thus, the hydrogen molecule is represented as

$$\mathrm{H}—\mathrm{H}$$

A formula such as this, which is drawn with Lewis symbols, is called a **Lewis formula** or **Lewis structure.** It is also called a **structural formula** because it shows which atoms are present in the molecule *and* how they are attached to each other.

The Octet Rule and Covalent Bonding

You have seen that when a nonmetal atom forms an anion, electrons are gained until the *s* and *p* subshells of its valence shell are completed. The tendency of a nonmetal atom to finish with a completed valence shell, usually consisting of eight electrons, also influences the number of electrons the atom tends to acquire by sharing, and it thereby affects the number of covalent bonds the atom forms.

Hydrogen, with just one electron in its 1*s* orbital, completes its valence shell by obtaining a share of just one electron from another atom, so a hydrogen atom forms just one covalent bond. When this other atom is hydrogen, the H_2 molecule is formed.

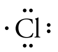
■ As you will see, it is useful to remember that hydrogen atoms form only one covalent bond.

Many atoms form covalent bonds by sharing enough electrons to give them complete *s* and *p* subshells in their outer shells. This is the noble gas configuration mentioned earlier and is the basis of the octet rule described in Section 9.3. As applied to covalent bonding, the **octet rule** can be stated as follows: *When atoms form covalent bonds, they tend to share sufficient electrons so as to achieve an outer shell having eight electrons.*

TOOLS

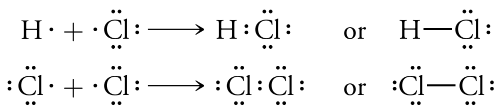
Octet rule and covalent bonding

Often, the octet rule can be used to explain the number of covalent bonds an atom forms. This number normally equals the number of electrons the atom must acquire to have a total of eight (an octet) in its outer shell. For instance, the halogens (Group 7A) all have seven valence electrons. The Lewis symbol for a typical member of this group, chlorine, is



$$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon$$

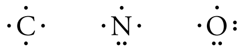
We can see that only one electron is needed to complete its octet. Of course, chlorine can actually gain this electron and become a chloride ion. This is what it does when it forms an ionic compound such as sodium chloride (NaCl). When chlorine combines with another nonmetal, however, the complete transfer of an electron is not energetically favorable. Therefore, in forming such molecules as HCl or Cl_2, chlorine gets the one electron it needs by forming a covalent bond.



$$\mathrm{H}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon \longrightarrow \mathrm{H}\colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon \quad \text{or} \quad \mathrm{H}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon$$

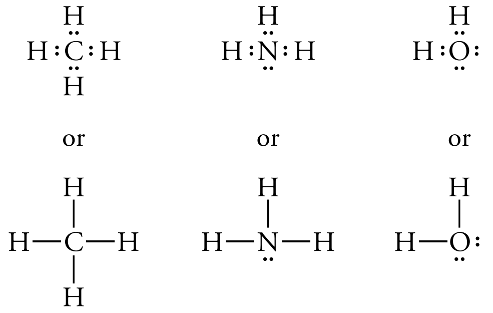
$$\colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon \longrightarrow \colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon \quad \text{or} \quad \colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\colon$$

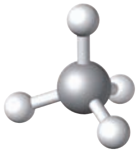
There are many nonmetals that form more than one covalent bond. For example, the three most important elements in biochemical systems are carbon, nitrogen, and oxygen.



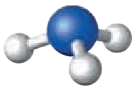
$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot \qquad \cdot\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}\cdot \qquad \cdot\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\colon$$

You've already encountered the simplest hydrogen compounds of these elements: methane, CH_4, ammonia, NH_3, and water, H_2O. Their Lewis structures are

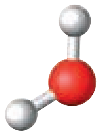




Methane



Ammonia



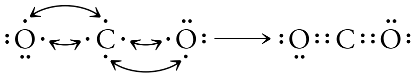
Water

In the ball-and-stick drawings of the molecules, the "sticks" represent the covalent bonds between the atoms.

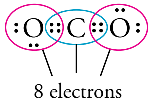
Multiple Bonds

The bond produced by the sharing of *one* pair of electrons between two atoms is called a **single bond**. So far, these have been the only kind we've discussed. There are, however, many molecules in which more than a single pair of electrons are shared between two atoms. For example, we can diagram the formation of the bonds in CO_2 as follows.

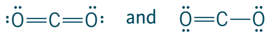
■ The arrows here simply indicate how the electrons can combine to form the electron pair bonds in the molecule.



The carbon atom shares two of its valence electrons with one oxygen and two with the other. At the same time, each oxygen shares two electrons with carbon. The result is the formation of two **double bonds.** Notice that in the Lewis formula, both of the shared electron pairs are placed between the symbols for the two atoms joined by the double bond. Once again, if we circle the valence shell electrons that "belong" to each atom, we see that each has an octet.

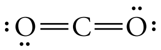


■ How we place the unshared pairs of electrons around the oxygen is unimportant. Two equally valid Lewis structure for CO_2 are



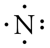
$:\ddot{O}=C=\ddot{O}:$ and $\underset{\cdot\cdot}{\ddot{O}}=C-\underset{\cdot\cdot}{\ddot{O}}$

The Lewis structure for CO_2, using dashes, is



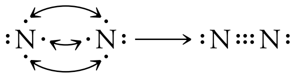
$$:\underset{\cdot\cdot}{O}=C=\ddot{O}:$$

Sometimes three pairs of electrons are shared between two atoms. The most abundant gas in the atmosphere, nitrogen, occurs in the form of diatomic molecules, N_2. As we've seen, the Lewis symbol for nitrogen is

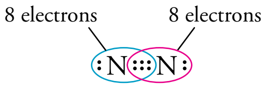


$$\cdot\overset{\cdot}{\underset{\cdot}{N}}:$$

and each nitrogen atom needs three electrons to complete its octet. When the N_2 molecule is formed, each of the nitrogen atoms shares three electrons with the other.



The result is called a **triple bond.** Again, notice that we place all three electron pairs of the bond between the two atoms. We count all of these electrons as though they belong to both of the atoms. Each nitrogen therefore has an octet.



The triple bond is usually represented by three dashes, so the bonding in the N_2 molecule is normally shown as

$$:N\equiv N:$$

9.6 | Covalent Compounds of Carbon

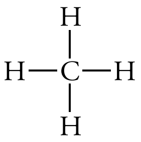
Covalent bonds are found in many of the substances we encounter on a daily basis. Most of them are classified as **organic compounds** in which carbon atoms are covalently bonded to other carbon atoms and to a variety of other nonmetals. They include the foods we eat, the fabrics we wear, the medicines that cure us, the fuels that power vehicles, and the fibers in the rope supporting the mountain climber in the opening photo of this chapter. Because they are so common, organic compounds will be used frequently as examples in our discussions later in the book. For this reason, you will find it helpful to learn something now about their makeup.

■ If you are also enrolled in a course in biology, you will find some knowledge of organic chemistry useful in understanding that subject as well.

Organic compounds fall into different classes according to the elements that are bonded to carbon and how atoms of those elements are arranged in the molecules. The kinds of compounds we will study in this section will include those in which carbon is bonded to hydrogen, oxygen, and nitrogen. As you learned in Chapter 3, such substances can be considered to be derived from hydrocarbons—compounds of carbon and hydrogen in which the basic molecular "backbones" are composed of carbon atoms linked to one another in a chainlike fashion. (Hydrocarbons themselves are the principal constituents of petroleum.)

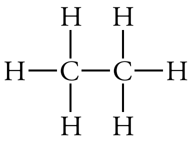
■ A more comprehensive discussion of organic compounds is found in Chapter 23. In this section we look at some simple ways carbon atoms combine with other atoms to form certain important classes of organic substances that we encounter frequently.

One of the chief features of organic compounds is the tendency of carbon to complete its octet by forming four covalent bonds. For example, in the alkane series of hydrocarbons (which we described briefly on page 92) all of the bonds are single bonds. The structures of the first three alkanes (methane, ethane, and propane) are



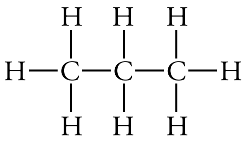
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

methane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethane



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

propane

■ These structures can be written in a condensed form as

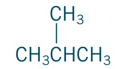
CH_4
CH_3CH_3
$CH_3CH_2CH_3$

The shapes of their molecules are illustrated as space-filling models in Figure 3.19 on page 93.

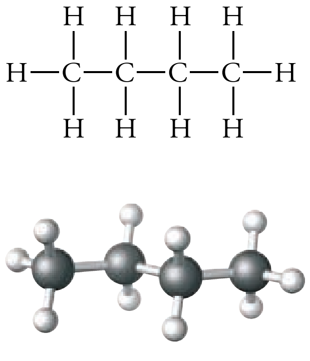
When more than four carbon atoms are present, matters become more complex because there is more than one way to arrange the atoms. For example, butane has the formula C_4H_{10}, but there are two ways to arrange the carbon atoms. These two arrangements occur in compounds commonly called butane and isobutane.

■ Butane and isobutane are said to be isomers of each other. In condensed form, we can write their structures as

$CH_3CH_2CH_2CH_3$

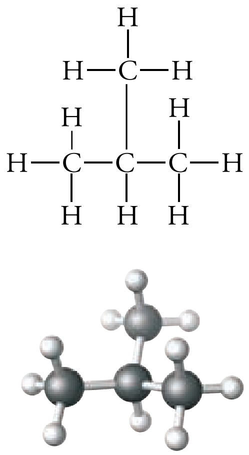


$$\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_3 \end{array}$$



Butane

C_4H_{10}
bp = –0.5 °C

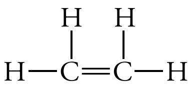


Methylpropane (isobutane)

C_4H_{10}
bp = –11.7 °C

Even though they have the same molecular formula, these are actually different compounds with different properties, as you can see from the boiling points listed below their structures. The ability of atoms to arrange themselves in more than one way to give different compounds that have the same molecular formula is called **isomerism** and is discussed more fully in Chapters 22 and 23. The existence of *isomers* is one of the reasons there are so many organic compounds. For example, there are 366,319 different compounds, or isomers, that have the formula $C_{20}H_{42}$; they differ only in the way the carbon atoms are attached to each other.

Carbon can also complete its octet by forming double or triple bonds. The Lewis structures of ethene, C_2H_4, and ethyne, C_2H_2 (commonly called ethylene and acetylene, respectively) are as follows:[4]



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & = & C & - & H \end{array}$$

ethene
(ethylene)

$$H{-}C{\equiv}C{-}H$$

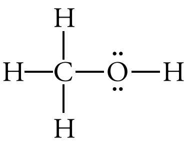
ethyne
(acetylene)

Compounds That Also Contain Oxygen and Nitrogen

Most organic compounds contain elements in addition to carbon and hydrogen. As we mentioned in Chapter 3, it is convenient to consider such compounds to be derived from hydrocarbons by replacing one or more hydrogens by other groups of atoms. Such compounds can be divided into various families according to the nature of the groups, called **functional groups,** attached to the parent hydrocarbon fragment. Some such families are summarized in Table 9.2, in which the hydrocarbon fragment to which the functional group is attached is symbolized by the letter R.

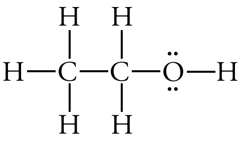
Alcohols

In Chapter 3 we noted that alcohols are organic compounds in which one of the hydrogen atoms of a hydrocarbon is replaced by OH. The family name for these compounds is **alcohol**. Examples are methanol (methyl alcohol) and ethanol (ethyl alcohol), which have the following structures:



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & \overset{..}{\underset{..}{O}} & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

methanol
(methyl alcohol)



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & \overset{..}{\underset{..}{O}} & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

ethanol
(ethyl alcohol)

sterno
BRAND
CANNED HEAT
from COLGATE-PALMOLIVE
COOKING FUEL
11140737

This container of "Canned Heat" contains methanol as the fuel. It is commonly used to heat food at buffets. *(Andy Washnik)*

Some **condensed formulas** that we might write for these are CH_3OH and CH_3CH_2OH, or $CH_3{-}OH$ and $CH_3CH_2{-}OH$. Methanol is used as a solvent and a fuel; ethanol is found in alcoholic beverages and is blended with gasoline to yield a fuel called E85, containing 85% ethanol.

Ketones

In alcohols, the oxygen forms two single bonds to complete its octet, just as in water. But oxygen can also form double bonds, as you saw for CO_2. One family of compounds in which a doubly bonded oxygen replaces a pair of hydrogen atoms is called **ketones.** The

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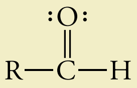
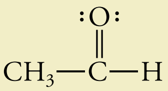
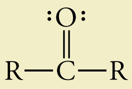
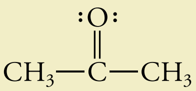
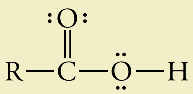
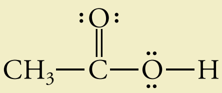
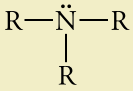
[4] In the IUPAC system for naming organic compounds, *meth-*, *eth-*, *prop-*, and *but-* indicate carbon chains of 1, 2, 3, and 4 carbon atoms, respectively. Organic nomenclature is discussed more fully in Chapter 23.

Table 9.2 Some Families of Oxygen- and Nitrogen-Containing Organic Compounds

Family Name	General Formula[a]	Example
Alcohols	$\mathrm{R-\underset{\cdot\cdot}{\ddot{O}}-H}$	$\mathrm{CH_3-\underset{\cdot\cdot}{\ddot{O}}-H}$ methanol
Aldehydes	 $\mathrm{R-\overset{\overset{:O:}{\Vert}}{C}-H}$	 $\mathrm{CH_3-\overset{\overset{:O:}{\Vert}}{C}-H}$ ethanal (acetaldehyde)
Ketones	 $\mathrm{R-\overset{\overset{:O:}{\Vert}}{C}-R}$	 $\mathrm{CH_3-\overset{\overset{:O:}{\Vert}}{C}-CH_3}$ propanone (acetone)
Acids	 $\mathrm{R-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H}$	 $\mathrm{CH_3-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H}$ ethanoic acid (acetic acid)
Amines	$\mathrm{R-\ddot{N}H_2}$ $\mathrm{R-\ddot{N}H-R}$  $\mathrm{R-\underset{\underset{R}{\vert}}{\ddot{N}}-R}$	$\mathrm{CH_3-\ddot{N}H_2}$ methylamine

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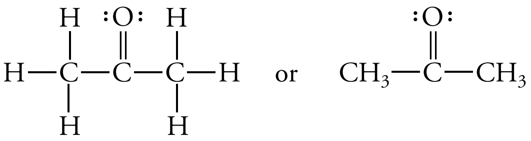
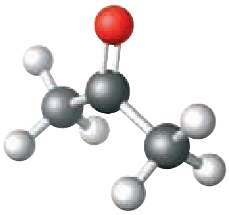
[a] R stands for a hydrocarbon fragment such as $\mathrm{CH_3}$— or $\mathrm{CH_3CH_2}$—.

simplest example is propanone, better known as acetone, a solvent often used in nail polish remover.



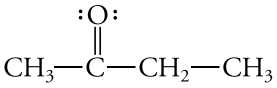
$$\begin{array}{ccccccc} & & \mathrm{H} & \mathrm{:O:} & \mathrm{H} & & \\ & & \vert & \Vert & \vert & & \\ \mathrm{H} & - & \mathrm{C} & -\mathrm{C}- & \mathrm{C} & - & \mathrm{H} \\ & & \vert & & \vert & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array} \quad \text{or} \quad \mathrm{CH_3-\overset{\overset{:O:}{\Vert}}{C}-CH_3}$$

propanone
(acetone)



Acetone

Ketones are found in many useful solvents that dissolve various plastics. An example is methyl ethyl ketone.

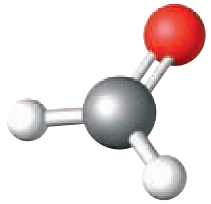


$$\mathrm{CH_3-\overset{\overset{:O:}{\Vert}}{C}-CH_2-CH_3}$$

butanone
(methyl ethyl ketone)

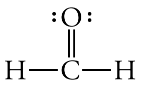
Aldehydes

Notice that in ketones the carbon bonded to the oxygen is also attached to *two* other carbon atoms. If at least one of the atoms attached to the C═O group (called a **carbonyl group,** pronounced *car-bon-EEL*) is a hydrogen, a different family of compounds is formed



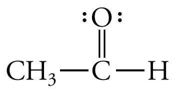
Formaldehyde

called **aldehydes.** Examples are formaldehyde (used to preserve biological specimens, for embalming, and to make plastics) and acetaldehyde (used in the manufacture of perfumes, dyes, plastics, and other products).



$$H-\overset{\overset{:\ddot{O}:}{\|}}{C}-H$$

methanal
(formaldehyde)

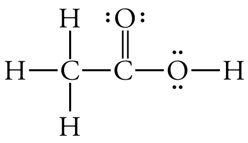


$$CH_3-\overset{\overset{:\ddot{O}:}{\|}}{C}-H$$

ethanal
(acetaldehyde)

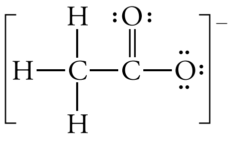
Organic Acids

Organic acids, also called **carboxylic acids,** constitute another very important family of oxygen-containing organic compounds. An example is acetic acid, which we described in Chapter 5. The shape of the molecule was illustrated in Figure 5.11 (page 165), showing the single hydrogen atom that is capable of ionizing in the formation of H_3O^+. The Lewis structures of acetic acid and the acetate ion are



$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}-H$$

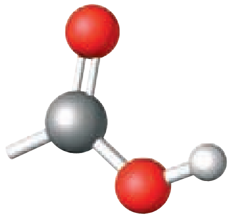
acetic acid



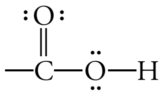
$$\left[H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}:\right]^-$$

acetate ion

In general, the structures of organic acids are characterized by the presence of the **carboxyl group,** $-CO_2H$.



The carboxyl group



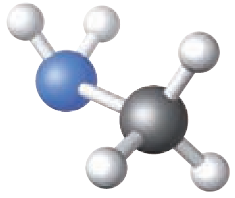
$$-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}-H$$

carboxyl group

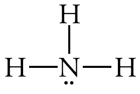
Notice that organic acids have both a doubly bonded oxygen and an OH group attached to the end carbon atom.

Amines

Nitrogen atoms need three electrons to complete an octet, and in most of its compounds, nitrogen forms three bonds. The common nitrogen-containing organic compounds can be imagined as being derived from ammonia by replacing one or more of the hydrogens of NH_3 with hydrocarbon groups. They're called amines, and an example is methylamine, CH_3NH_2.

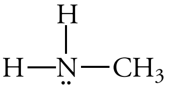


Methylamine



$$H-\underset{..}{\overset{\overset{H}{|}}{N}}-H$$

ammonia



$$H-\underset{..}{\overset{\overset{H}{|}}{N}}-CH_3$$

methylamine

Amines are strong-smelling compounds and often have a "fishy" odor. Like ammonia, they're weakly basic.[5]

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

As we noted in Chapter 5, the H^+ that is added to an amine becomes attached to the nitrogen atom.

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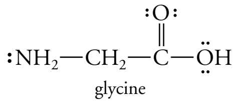
[5] Amino acids, which are essential building blocks of proteins in our bodies, contain both an amine group ($-NH_2$) and a carboxyl group ($-CO_2H$). The simplest of these is the amino acid glycine,

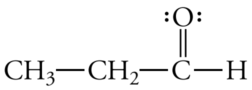


$$:NH_2-CH_2-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}H$$

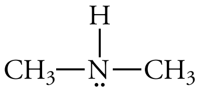
glycine

Practice Exercises

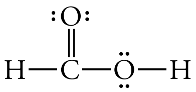
9.6 | Match the structural formulas on the left with the correct names of the families of organic compounds to which they belong.



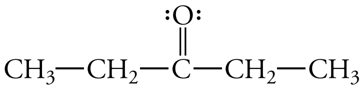
$$CH_3-CH_2-\overset{\overset{:O:}{\|}}{C}-H$$



$$CH_3-\overset{\overset{H}{|}}{\underset{..}{N}}-CH_3$$



$$H-\overset{\overset{:O:}{\|}}{C}-\underset{..}{\ddot{O}}-H$$



$$CH_3-CH_2-\overset{\overset{:O:}{\|}}{C}-CH_2-CH_3$$

$CH_3-CH_2-CH_2-\underset{..}{\ddot{O}}-H$

amine

alcohol

ketone

aldehyde

acid

9.7 | The following questions apply to the compounds in Practice Exercise 9.6. (a) Which produces a basic solution in water? (b) Which produces an acidic aqueous solution? (c) For the acid, what is the Lewis structure of the anion formed when it is neutralized?

9.7 | Bond Polarity and Electronegativity

When two identical atoms form a covalent bond, as in H_2 or Cl_2, each atom has an equal share of the bond's electron pair. The electron density at both ends of the bond is the same, because the electrons are equally attracted to both nuclei. However, when different kinds of atoms combine, as in HCl, one nucleus usually attracts the electrons in the bond more strongly than the other.

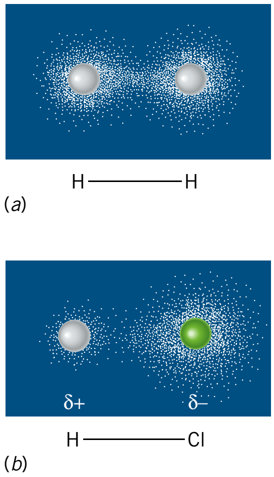
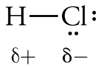


Figure 9.8 | **Equal and unequal sharing of electrons in a covalent bond.** Each of the diagrams illustrate the distribution of electron density of the shared electron pair in a bond. (*a*) In H_2, the electron density in the bond is spread equally over both atoms. (*b*) In HCl, more than half of the electron density of the bond is concentrated around chlorine, causing opposite ends of the bond to carry partial electrical charges.

Polar and Nonpolar Bonds

The result of unequal attractions for the bonding electrons is an unbalanced distribution of electron density within the bond. For example, chlorine atoms have a greater attraction for electrons in a bond than do hydrogen atoms. In the HCl molecule, therefore, the electron cloud is pulled more tightly around the Cl, and that end of the molecule experiences a slight buildup of negative charge. The electron density that shifts toward the chlorine is removed from the hydrogen, which causes the hydrogen end to acquire a slight positive charge. These charges are less than full 1+ and 1− charges and are called **partial charges,** which are usually indicated by the lowercase Greek letter delta, δ (see Figure 9.8). Partial charges can also be indicated on Lewis structures. For example,



$$\underset{\delta+}{H}-\underset{\delta-}{\underset{..}{\ddot{Cl}}:}$$

A bond that carries partial positive and negative charges on opposite ends is called a **polar covalent bond,** or often simply a **polar bond** (the word *covalent* is understood). The term *polar* comes from the notion of *poles* of equal but opposite charge at either end of the bond. Because *two poles* of electric charge are involved, the bond is said to be an **electric dipole.**

The polar bond in HCl causes the molecule as a whole to have opposite charges on either end, so the HCl molecule as a whole is an electric dipole. We say that HCl is a **polar molecule.** The magnitude of its polarity is expressed quantitatively by its **dipole moment** (symbol μ), which is equal to the amount of charge on either end of the molecule, q, multiplied by the distance between the charges, r.

Dipole moment

$$\mu = q \times r \tag{9.2}$$[6]

Table 9.3 lists the dipole moments and bond lengths for some diatomic molecules. The dipole moments are reported in **debye** units (symbol D), where 1 D = 3.34×10^{-30} C m (coulomb × meter).

By separate experiments, it is possible to measure both μ and r (which corresponds to the bond length in a diatomic molecule such as HCl). Knowledge of μ and r makes it possible to calculate the amount of charge on opposite ends of the dipole. For HCl, such calculations show that q equals 0.17 electronic charge units, which means the hydrogen carries a charge of $+0.17e^-$ and the chlorine a charge of $-0.17e^-$.

Table 9.3 Dipole Moments and Bond Lengths for Some Diatomic Molecules[a]

Compound	Dipole Moment (D)	Bond Length (pm)
HF	1.83	91.7
HCl	1.09	127
HBr	0.82	141
HI	0.45	161
CO	0.11	113
NO	0.16	115

[a] Source: National Institute of Standards and Technology.

One of the main reasons we are concerned about whether a molecule is polar or not is because many physical properties, such as melting point and boiling point, are affected by it. This is because polar molecules attract each other more strongly than do nonpolar molecules. The positive end of one polar molecule attracts the negative end of another. The strength of the attraction depends on both the amount of charge on either end of the molecule and the distance between the charges; in other words, it depends on the molecule's dipole moment.

Example 9.5
Calculating the Charge on the End of a Polar Molecule

The HF molecule has a dipole moment of 1.83 D and a bond length of 91.7 pm. What is the amount of charge, in electronic charge units, on either end of the bond?

■ **Analysis:** This is going to involve substituting values into Equation 9.2. However, to answer the problem correctly, we will have to be especially careful of the units. The debye has charge expressed in coulombs, but we have to express the answer in electronic charge units.

■ **Assembling the Tools:** The primary tool for solving the problem is Equation 9.2. In the calculation we are also going to have to convert between coulombs (C) and electronic charge units. From the table on the inside rear cover of the book we find that the charge on an electron (i.e., an electronic charge unit) equals 1.602×10^{-19} C, which we can express as

$$1\ e^- \Leftrightarrow 1.602 \times 10^{-19}\ \mathrm{C}$$

■ **Solution:** We will solve Equation 9.2 for q.

$$q = \frac{\mu}{r}$$

The debye unit, D, = 3.34×10^{-30} C m, so the dipole moment of HF is

$$\mu = (1.83\ \cancel{\mathrm{D}})\ (3.34 \times 10^{-30}\ \mathrm{C\ m}/\cancel{\mathrm{D}}) = 6.11 \times 10^{-30}\ \mathrm{C\ m}$$

---

[6] Once again, we're using the symbol q to mean electric charge, not heat as in Chapter 7.

The SI prefix p (pico) means × 10^{-12}, so the bond length $r = 91.7 \times 10^{-12}$ m. Substituting in the equation above gives

$$q = \frac{6.11 \times 10^{-30}\ \text{C}\ \cancel{\text{m}}}{91.7 \times 10^{-12}\ \cancel{\text{m}}} = 6.66 \times 10^{-20}\ \text{C}$$

The value of q in electronic charge units is therefore

$$q = 6.66 \times 10^{-20}\ \cancel{\text{C}} \times \left(\frac{1\ e^-}{1.602 \times 10^{-19}\ \cancel{\text{C}}}\right) = 0.416\ e^-$$

As in HCl, the hydrogen carries the positive charge, so the charge on the hydrogen end of the molecule is $+0.416\ e^-$ and the charge on the fluorine end is $-0.416\ e^-$.

Is the Answer Reasonable? If we look at the units, we see that they cancel correctly, so that gives us confidence that we've done the calculation correctly. The fact that our answer is between zero and one electronic charge unit, and therefore a partial electrical charge, further suggests we've solved the problem correctly.

Practice Exercises

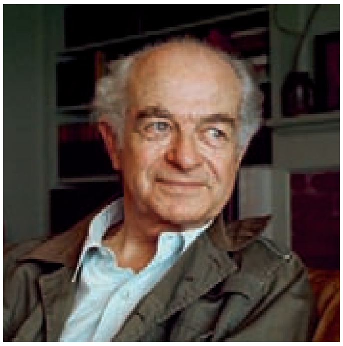
9.8 | The chlorine end of the chlorine monoxide molecule carries a charge of $+0.167\ e^-$. The bond length is 154.6 pm. Calculate the dipole moment of the molecule in debye units. (*Hint:* Be sure to convert the charge to coulombs.)

9.9 | Although isolated Na^+ and Cl^- ions are unstable, these ions can exist in the gaseous state as *ion pairs*. An ion pair consists of an NaCl unit in which the bond length is 236 pm. The dipole moment of the ion pair is 9.00 D. What are the actual amounts of charge on the sodium and chlorine atoms in this NaCl pair? What percentage of full 1+ and 1− charges are these? (This is the *percentage ionic character* in the NaCl pair.)

Electronegativity

The degree to which a covalent bond is polar depends on the difference in the abilities of the bonded atoms to attract electrons. The greater the difference, the more polar the bond, and the more the electron density is shifted toward the atom that attracts electrons more.

The term that we use to describe the attraction an atom has for the electrons in a bond is called **electronegativity.** In HCl, for example, chlorine is *more electronegative* than hydrogen. This causes the electron pair of the covalent bond to spend more of its time around the more electronegative atom, which is why the Cl end of the bond acquires a partial negative charge.



Linus Pauling (1901–1994) contributed greatly to our understanding of chemical bonding. He was the winner of two Nobel Prizes, in 1954 for chemistry and in 1962 for peace. *(Ted Streshinsky/© Corbis)*

The first scientist to develop numerical values for electronegativity was Linus Pauling (1901–1994). He observed that polar bonds have a bond energy larger than would be expected if the opposite ends of the bonds were electrically neutral. Pauling reasoned that the extra bond energy is caused by the attraction between the partial charges on opposite ends of the bond. By estimating the extra bond energy, he was able to develop a scale of electronegativities for the elements. Other scientists have used different approaches to measuring electronegativities, with similar results.

A set of numerical values for the electronegativities of the elements is shown in Figure 9.9. These data are useful because the *difference* in electronegativity provides an estimate of the degree of polarity of a bond. For instance, the data tell us fluorine is more electronegative than chlorine, so we expect HF to be more polar than HCl. (This is confirmed by the larger dipole moment of the HF molecule.) In addition, the relative magnitudes of the electronegativities indicate which ends of a bond carry the partial positive and negative charges. Thus, hydrogen is less electronegative than

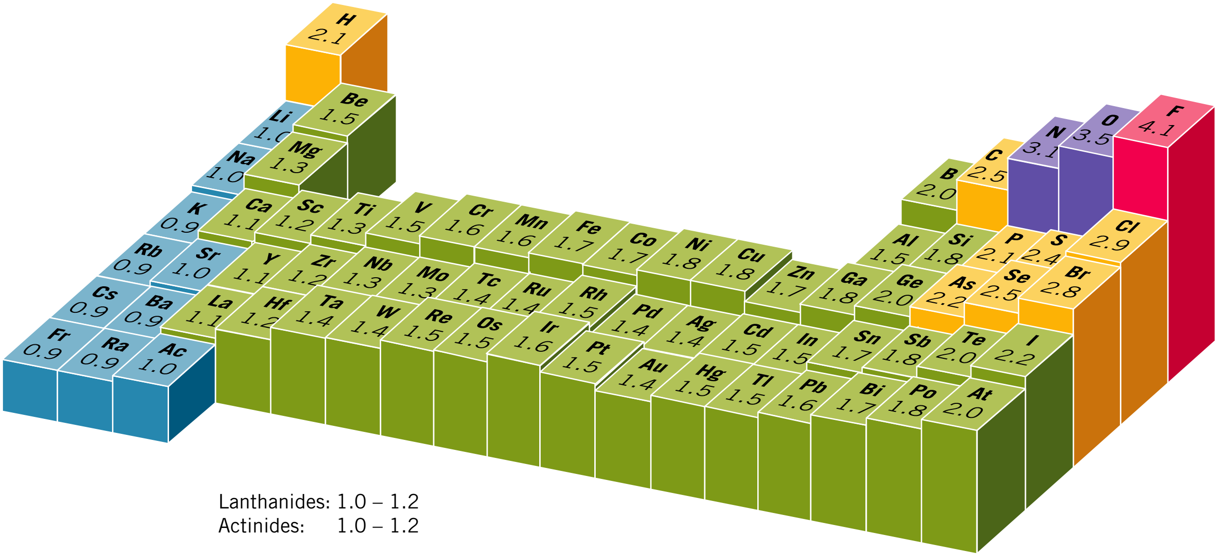


Figure 9.9 | **The electronegativities of the elements.** The noble gases are assigned electronegativities of zero and are omitted from the table.

either fluorine or chlorine, so in both of these molecules the hydrogen bears the partial positive charge.

$$\underset{\delta+}{\mathrm{H}}\text{—}\underset{\delta-}{\ddot{\mathrm{F}}}\!:\qquad \underset{\delta+}{\mathrm{H}}\text{—}\underset{\delta-}{\ddot{\mathrm{Cl}}}\!:$$

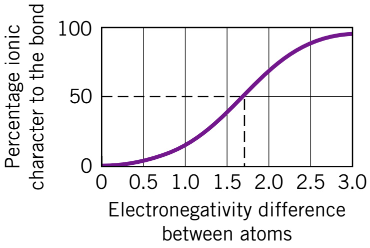


Figure 9.10 | **Variation in the percentage ionic character of a bond with electronegativity difference.** The bond becomes about 50% ionic when the electronegativity difference equals 1.7, which means that the atoms in the bond carry a partial charge of approximately ± 0.5 e^-.

By studying electronegativity values and their differences we find that there is no sharp dividing line between ionic and covalent bonding. Ionic bonding and *nonpolar covalent bonding* simply represent the two extremes. A bond is mostly ionic when the difference in electronegativity between two atoms is very large; the more electronegative atom acquires essentially complete control of the bonding electrons. In a **nonpolar covalent bond,** there is no difference in electronegativity, so the pair of bonding electrons is shared equally.

$$\mathrm{Cs}^+\left[:\ddot{\underset{..}{\mathrm{F}}}:\right]^- \qquad :\ddot{\underset{..}{\mathrm{F}}}:\ddot{\underset{..}{\mathrm{F}}}:$$

"bonding pair" held exclusively by fluorine

bonding pair shared equally

The degree to which the bond is polar, which we might think of as the amount of **ionic character** of the bond, varies in a continuous way with changes in the electronegativity difference (Figure 9.10). The bond becomes more than 50% ionic when the electronegativity difference exceeds approximately 1.7.

Practice Exercises

9.10 | Bromine and chlorine form a molecular substance with the formula BrCl. Is the bond polar? If so, which atom carries the partial negative charge? (*Hint:* Compare electronegativities.)

9.11 | For each of the following bonds, choose the atom that carries the partial negative charge. Arrange them in order of increasing bond polarity: (a) P—Br, (b) Si—Cl, (c) S—Cl.

Periodic Trends in Electronegativity

An examination of Figure 9.9 reveals that within the periodic table, *electronegativity increases from bottom to top in a group, and from left to right in a period.* These trends follow those for ionization energy (IE); an atom that has a small IE will lose an electron more easily than an atom with a large IE, just as an atom with a small electronegativity will lose its share of an electron pair more readily than an atom with a large electronegativity.

TOOLS

Periodic trends in electronegativity

Elements located in the same region of the table (for example, the nonmetals) have similar electronegativities, which means that if they form bonds with each other, the electronegativity differences will be small and the bonds will be more covalent than ionic. On the other hand, if elements from widely separated regions of the table combine, large electronegativity differences occur and the bonds will be predominantly ionic. This is what happens, for example, when an element from Group 1A or Group 2A reacts with a nonmetal from the upper right-hand corner of the periodic table.

■ It is found that the electronegativity is proportional to the average of the ionization energy and the electron affinity of an element.

Reactivities of the Elements and Electronegativity

There are parallels between an element's electronegativity and its **reactivity**—its tendency to undergo redox reactions.

Reactivities of Metals Relate to Their Ease of Oxidation

In nearly every compound containing a metal, the metal exists in a positive oxidation state. Therefore, for a metal, *reactivity* relates to how easily the metal is oxidized. For example, a metal like sodium, which is very easily oxidized, is said to be very reactive, whereas a metal like platinum, which is very difficult to oxidize, is said to be unreactive.

■ *Reactivity* refers in general to the tendency of a substance to react with something. The *reactivity of a metal* refers to its tendency specifically to undergo *oxidation*.

There are several ways to compare how easily metals are oxidized. In Chapter 6 we saw that by comparing the abilities of metals to displace each other from compounds we are able to establish their relative ease of oxidation. This was the basis for the activity series (Table 6.3).

Figure 9.11 illustrates how the ease of oxidation (reactivity) of metals varies in the periodic table. In general, these trends roughly follow the variations in electronegativity, with the metal being less easily oxidized as its electronegativity increases. You might expect this, because electronegativity is a measure of how strongly the atom of an element attracts electrons when combining with an atom of a different element. The more strongly the atom attracts electrons, the more difficult it is to oxidize. This relationship between reactivity and electronegativity is only approximate, however, because many other factors affect the stability of the compounds that are formed.

TOOLS

Trends in the reactivity of metals in the periodic table

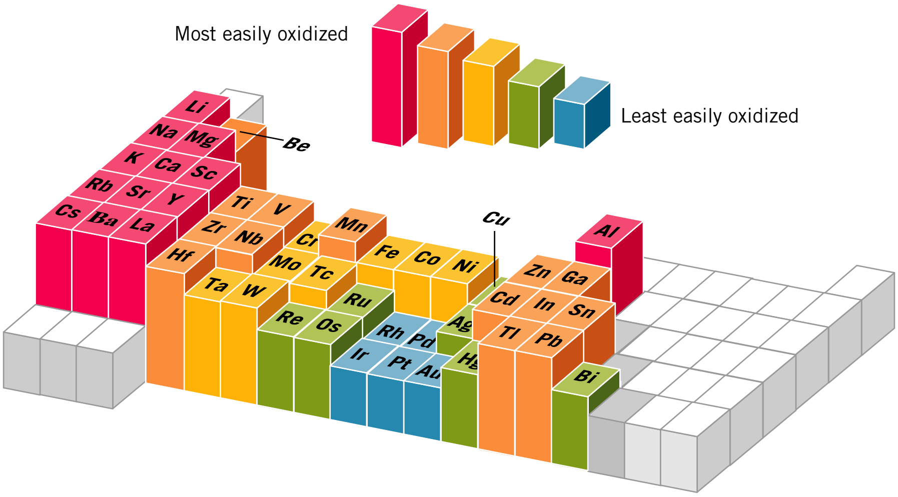


Figure 9.11 | **Variations in the ease of oxidation of metals.**

Elements of Groups 1A and 2A

In Figure 9.11, we see that the metals that are most easily oxidized are found at the far left in the periodic table. These are elements with very low electronegativities. The metals in Group 1A, for example, are so easily oxidized that all of them react with water to liberate hydrogen. Because of their reactivity toward moisture and oxygen, they have no useful applications that require exposure to the atmosphere, so we rarely encounter them as free metals. The same is true of the heavier metals in Group 2A, calcium through barium. These elements also react with water to liberate hydrogen. In Figure 9.9 we see that electronegativity decreases going down a group, which explains why the heavier elements in Group 2A are more reactive than those at the top of the group.

Noble Metals

In Figure 9.11 we can also locate the metals that are the most difficult to oxidize. They occur for the most part among the heavier transition elements in the center of the periodic table. Here we find the elements platinum and gold, which are sometimes called **noble metals** because of their extremely low degree of reactivity. Their bright luster and lack of any tendency to corrode in air or water combine to make them particularly attractive for use in fine jewelry. Their lack of reactivity also is responsible for their industrial uses. Gold, for example, is used to coat the electrical contacts in low-voltage circuits found in microcomputers, because even a small amount of corrosion on a more reactive metal would be sufficient to impede the flow of electricity so much as to make the devices unreliable.

This statue of Prometheus overlooking the skating rink in Rockefeller Center in New York City is covered in a thin layer of gold, providing both beauty and weather resistance. *(Philipus/Alamy)*

The Oxidizing Power of Nonmetals

The reactivity of a nonmetal is determined by its ease of reduction, and therefore its ability to serve as an oxidizing agent. This ability also varies according to the element's electronegativity. Nonmetals with high electronegativities have strong tendencies to acquire electrons and are therefore strong oxidizing agents. In parallel with changes in electronegativities in the periodic table, *the oxidizing abilities of nonmetals increase from left to right across a period and from bottom to top in a group.* Thus, the most powerful oxidizing agent is fluorine, followed closely by oxygen, both of which appear in the upper right-hand corner of the periodic table.

TOOLS

Trends in the reactivity of nonmetals in the periodic table

Single replacement reactions (also called **displacement reactions**) occur among the nonmetals, just as with the metals (which you studied in Chapter 6). For example, heating a metal sulfide in oxygen causes the sulfur to be replaced by oxygen. The displaced sulfur then combines with additional oxygen to give sulfur dioxide. The equation for a typical reaction is

$$\mathrm{CuS}(s) + \tfrac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CuO}(s) + \mathrm{SO_2}(g)$$

Displacement reactions are especially evident among the halogens, where a particular halogen in its elemental form will oxidize the *anion* of any halogen below it in Group 7A, as illustrated in the margin. Thus, F_2 will oxidize Cl^-, Br^-, and I^-; Cl_2 will oxidize Br^- and I^-, but not F^-; and Br_2 will oxidize I^-, but not F^- or Cl^-.

- Fluorine:

$$F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$$
$$F_2 + 2Br^- \longrightarrow 2F^- + Br_2$$
$$F_2 + 2I^- \longrightarrow 2F^- + I_2$$

Chlorine:

$$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$$
$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$

Bromine:

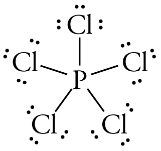
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

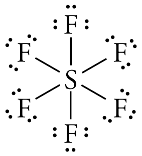
9.8 | Lewis Structures

In Section 9.5 we introduced you to Lewis structures and we have used them to describe various molecules, all of which obey the octet rule. Examples included CO_2, Cl_2, N_2, as well as a variety of organic compounds.

Lewis structures are very useful in chemistry because they give us a relatively simple way to describe the structures of molecules. As a result, much chemical reasoning is based on them. In fact, in Chapter 10 you will learn how to use Lewis structures to make reasonably accurate predictions about the shapes of molecules. In this section we will develop a simple method for drawing Lewis structures for both molecules and polyatomic ions (which are also held together by covalent bonds).

Although the octet rule is important in covalent bonding, it is not always obeyed. For instance, there are some molecules in which one or more atoms must have more than an octet in the valence shell. Examples are PCl_5 and SF_6, whose Lewis structures are

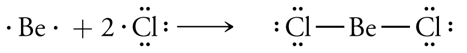




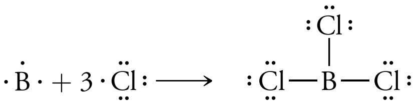
■ Lewis structures just describe which atoms are bonded to each other and the kinds of bonds involved. Thus, the Lewis structure for water can be drawn as H—$\ddot{\underset{..}{\text{O}}}$—H, but it does not mean the water molecule is linear, with all the atoms in a straight line. Actually, water isn't linear; the two O—H bonds form an angle of about 104°.

In these molecules the formation of more than four bonds to the central atom requires that the central atom have a share of more than eight electrons.

There are also some molecules (but not many) in which the central atom behaves as though it has less than an octet. The most common examples involve compounds of beryllium and boron.



four electrons around Be



six electrons around B

■ Although beryllium is a metal, many of its compounds are not ionic. Pure $BeCl_2$ is molecular with covalent Be—Cl bonds.

Although Be and B sometimes have less than an octet, *the elements in Period 2 never* ***exceed*** *an octet.* The reason is because their valence shells, having $n = 2$, can hold a maximum of only 8 electrons. (This explains why the octet rule works so well for atoms of carbon, nitrogen, and oxygen.) However, elements in periods below Period 2, such as phosphorus and sulfur, sometimes do exceed an octet, because their valence shells can hold more than 8 electrons. For example, the valence shell for elements in Period 3, for which $n = 3$, could hold a maximum of 18 electrons, and the valence shell for Period 4 elements, which have *s*, *p*, *d*, and *f* subshells, could theoretically hold as many as 32 electrons.

A Procedure for Drawing Lewis Structures

TOOLS

Method for drawing Lewis structures

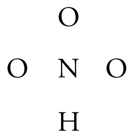
Figure 9.12 outlines a series of steps that provides a systematic method for drawing Lewis structures. The first step is to decide which atoms are bonded to each other, so that we know where to put the dots or dashes. This is not always a simple matter. Many times the formula suggests the way the atoms are arranged because the central atom, which is usually the least electronegative one, is usually written first. Examples are CO_2 and ClO_4^-, which have the following **skeletal structures** (i.e., arrangements of atoms):

$$\text{O}\quad\text{C}\quad\text{O}\qquad\qquad\begin{array}{ccc} & \text{O} & \\ \text{O} & \text{Cl} & \text{O} \\ & \text{O} & \end{array}$$

Sometimes, obtaining the skeletal structure is not quite so simple, especially when more than two elements are present. Some generalizations are possible, however. For example, the skeletal structure of nitric acid, HNO_3, is

$$\begin{array}{cccc} & & \text{O} & \\ \text{H} & \text{O} & \text{N} & \text{O} \end{array}\qquad\text{(correct)}$$

rather than one of the following:



$$\begin{array}{ccc} & \mathrm{O} & \\ \mathrm{O} & \mathrm{N} & \mathrm{O} \\ & \mathrm{H} & \end{array}$$

or H O O N O (incorrect)

Nitric acid is an oxoacid (Section 5.4), and it happens that the hydrogen atoms that can be released from molecules of oxoacids are always bonded to oxygen atoms, which are in turn bonded to the third nonmetal atom. Therefore, recognizing HNO_3 as the formula of an oxoacid allows us to predict that the three oxygen atoms are bonded to the nitrogen, and the hydrogen is bonded to one of the oxygens. (It is also useful to remember that hydrogen forms only one bond, so we should not choose it to be a central atom.)

There are times when no reasonable basis can be found for choosing a particular skeletal structure. If you must make a guess, choose the most symmetrical arrangement of atoms, because it has the greatest chance of being correct.

After you've decided on the skeletal structure, the next step is to count all of the *valence electrons* to find out how many dots must appear in the final formula. Using the periodic table, locate the groups in which the elements in the formula occur to determine the number of valence electrons contributed by each atom. If the structure you wish to draw is that of an ion, *add one additional valence electron for each negative charge or remove a valence electron for each positive charge*. Some examples are as follows:

SO_3	Sulfur (Group 6A) contributes $6e^-$.	$1 \times 6 = 6e^-$
	Each oxygen (Group 6A) contributes $6e^-$.	$3 \times 6 = 18e^-$
		Total $24e^-$
ClO_4^-	Chlorine (Group 7A) contributes $7e^-$.	$1 \times 7 = 7e^-$
	Each oxygen (Group 6A) contributes $6e^-$.	$4 \times 6 = 24e^-$
	Add $1e^-$ for the 1− charge.	$+1e^-$
		Total $32e^-$
NH_4^+	Nitrogen (Group 5A) contributes $5e^-$.	$1 \times 5 = 5e^-$
	Each hydrogen (Group 1A) contributes $1e^-$.	$4 \times 1 = 4e^-$
	Subtract $1e^-$ for the 1+ charge.	$-1e^-$
		Total $8e^-$

After we have determined the number of valence electrons, we place them into the skeletal structure in pairs following the steps outlined in Figure 9.12. Let's look at some examples of how we go about this.

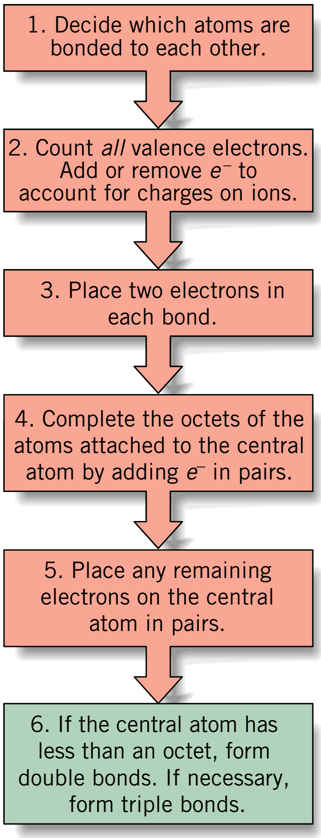
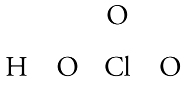

1. Decide which atoms are bonded to each other.
2. Count *all* valence electrons. Add or remove e⁻ to account for charges on ions.
3. Place two electrons in each bond.
4. Complete the octets of the atoms attached to the central atom by adding e⁻ in pairs.
5. Place any remaining electrons on the central atom in pairs.
6. If the central atom has less than an octet, form double bonds. If necessary, form triple bonds.

Figure 9.12 | **Summary of the steps in drawing a Lewis structure.** If you follow these steps, you will obtain a Lewis structure in which the octet rule is obeyed by the maximum number of atoms.

Example 9.6
Drawing Lewis Structures

What is the Lewis structure of the chloric acid molecule, $HClO_3$?

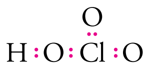
Analysis: The first step is to select a reasonable skeletal structure. Because the substance is an oxoacid, we can expect the hydrogen to be bonded to an oxygen, which in turn is bonded to the chlorine. The other two oxygens would also be bonded to the chlorine. This gives



$$\begin{array}{cccc} & & \mathrm{O} & \\ \mathrm{H} & \mathrm{O} & \mathrm{Cl} & \mathrm{O} \end{array}$$

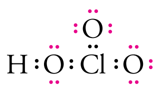
Assembling the Tools: Our tool is the procedure outlined in Figure 9.12.

Solution: The total number of valence electrons is 26 ($1e^-$ from H, $6e^-$ from each O, and $7e^-$ from Cl). To distribute the electrons, we start by placing a pair of electrons in each bond, because we know that there must be at least one pair of electrons between each pair of atoms.

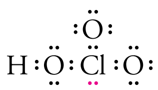


This has used $8e^-$, so we still have $18e^-$ to go. Next, we work on the atoms surrounding the chlorine (which is the central atom in this structure). No additional electrons are needed around the H, because $2e^-$ are all that can occupy its valence shell. Therefore, we next complete the octets of the oxygens, which uses 16 more electrons.

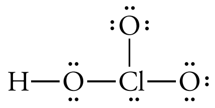
The valence shell of hydrogen contains only the 1*s* subshell, which can hold a maximum of two electrons. This means hydrogen can have a share of only two electrons and can form just one covalent bond.



We have now used a total of $24e^-$, so there are two electrons left. "Left-over" electrons are always placed on the central atom in pairs (the Cl atom, in this case). This gives



which we can also write as follows, using dashes for the electron pairs in the bonds:



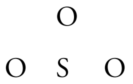
The chlorine and the three oxygens have octets, and the valence shell of hydrogen is complete with $2e^-$, so we are finished.

Is the Answer Reasonable? The most common error is to have either too many or too few valence electrons in the structure, so that's always the best place to begin your check. Doing this will confirm that the number of e^- is correct.

Example 9.7
Drawing Lewis Structures

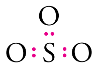
Draw the Lewis structure for the SO_3 molecule.

Analysis: Sulfur is less electronegative than oxygen and it is written first in the formula, so we expect it to be the central atom, surrounded by the three O atoms. This gives the skeletal structure

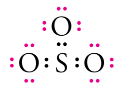


Assembling the Tools: We follow the procedure in Figure 9.12.

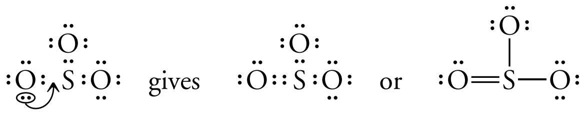
Solution: The total number of electrons in the formula is 24 ($6e^-$ from the sulfur, plus $6e^-$ from each oxygen). We begin to distribute the electrons by placing a pair in each bond. This gives



We have used $6e^-$, so there are $18e^-$ left. We next complete the octets around the oxygens, which uses the remaining electrons.



At this point all of the electrons have been placed into the structure, but we see that the sulfur has only six electrons around it. We cannot simply add more dots because the total must be 24. Therefore, according to the last step of the procedure in Figure 9.12, we have to create a multiple bond. *To do this we move a pair of electrons that we have shown to belong solely to an oxygen into a sulfur–oxygen bond so that it can be counted as belonging to both the oxygen and the sulfur.* In other words, we place a double bond between sulfur and one of the oxygens. It doesn't matter which oxygen we choose for this honor.



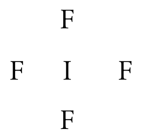
Notice that each atom has an octet.

Is the Answer Reasonable? The key step in completing the structure is recognizing what we have to do to obtain an octet around the sulfur. We have to add more electrons to the valence shell of sulfur, but without removing them from any of the oxygen atoms. By forming the double bond, we accomplish this. A quick check also confirms that we've placed exactly the correct number of valence electrons into the structure.

Example 9.8
Drawing Lewis Structures

What is the Lewis structure for the ion IF_4^-?

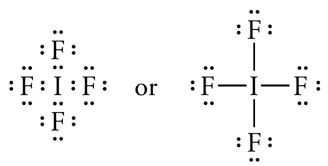
Analysis: Iodine is less electronegative than fluorine and is first in the formula, so we can anticipate that iodine will be the central atom. Our skeletal structure is



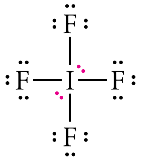
Assembling the Tools: As before, we follow the procedure in Figure 9.12. We begin by counting valence electrons, remembering to add an extra electron to account for the negative charge. Then we distribute the electrons in pairs.

Solution: The iodine and fluorine atoms are in Group 7A and each contribute 7 electrons, for a total of $35e^-$. The negative charge requires one additional electron to give a total of $36e^-$.

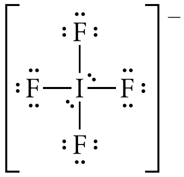
First we place $2e^-$ into each bond, and then we complete the octets of the fluorine atoms. This uses 32 electrons.



There are four electrons left, and according to Step 5 in Figure 9.12 they are placed on the central atom as *pairs* of electrons. This gives



The last step is to add brackets around the formula and write the charge outside as a superscript.



Is the Answer Reasonable? We can recount the valence electrons, which tells us we have the right number of them, and all are in the Lewis structure. Each fluorine atom has an octet, which is proper. Notice that we have placed the "left-over" electrons onto the central atom. This gives iodine more than an octet, but that's okay because iodine is not a Period 2 element.

Practice Exercises

9.12 | Predict a reasonable skeletal structure for $H_2PO_4^-$ and determine the number of valence electrons that should be in its Lewis structure. (*Hint:* It's an ion derived from an oxoacid.)

9.13 | Predict reasonable skeletal structures for SO_2, NO_3^-, $HClO_3$, and H_3AsO_4.

9.14 | How many valence electrons should appear in the Lewis structures of SO_2, SeO_4^{2-}, and NO^+?

9.15 | Draw Lewis structures for OF_2, NH_4^+, SO_2, NO_3^-, ClF_3, and $HClO_4$.

Formal Charges and Lewis Structures

Lewis structures are meant to describe how atoms share electrons in chemical bonds. Such descriptions are theoretical explanations or predictions that relate to the forces that hold molecules and polyatomic ions together. But, as you learned in Chapter 1, a theory is only as good as the observations on which it is based, so to have confidence in a theory about chemical bonding, we need to have a way to check it. We need experimental observations that relate to the description of bonding.

Bond Properties That Depend on Bond Order

To compare bonds between the same two elements, it's useful to define a quantity called the **bond order,** *which is the number of electron pairs shared between two atoms.* Thus, a single bond has a bond order of one, a double bond a bond order of two, and a triple bond a bond order of three.

Two properties that are related to the bond order are *bond length,* the distance between the nuclei of the bonded atoms, and *bond energy,* the energy required to separate the bonded atoms to give neutral particles. For example, we mentioned in Section 9.5 that measurements have shown the H_2 molecule has a bond length of 75 pm and a bond energy of 435 kJ/mol, which means that it takes 435 kJ to break the bonds of 1 mol of H_2 molecules to give 2 mol of hydrogen atoms.

Bond order is a measure of the amount of electron density in the bond, and the greater the electron density, the more tightly the nuclei are held and the more closely they are drawn together. This is illustrated by the data in Table 9.4, which gives typical bond lengths and bond energies for single, double, and triple bonds between carbon atoms. In summary:

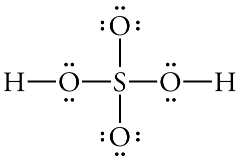
Table 9.4 Average Bond Lengths and Bond Energies Measured for Carbon–Carbon Bonds

Bond	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	154	348
C═C	134	615
C≡C	120	812

Correlation between bond properties and bond order

> As the bond order increases, the bond length decreases and the bond energy increases, provided we are comparing bonds between the same elements.

With this as background, let's examine the Lewis structure of sulfuric acid, drawn according to the procedure given in Figure 9.12.



(Structure I)

It obeys the octet rule, and there doesn't seem to be any need to attempt to write any other structures for it. But a problem arises if we compare the predicted bond lengths with those found experimentally. In our Lewis structure, all four sulfur–oxygen bonds are shown as single bonds, which means they should have about the same bond lengths. However, experimentally it has been found that the bonds are not of equal length, as illustrated in Figure 9.13. The S—O bonds are shorter than the S—OH bonds, which means they must have a larger bond order. Therefore, we need to modify our Lewis structure to make it conform to reality.

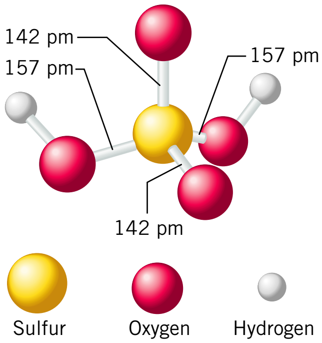
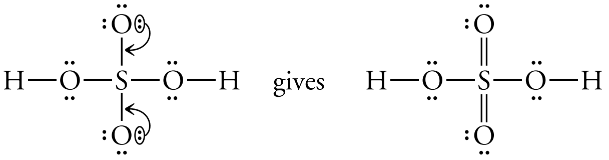


Figure 9.13 | **The structure of sulfuric acid in the vapor state.** Notice the difference in the sulfur–oxygen bond lengths.

Because sulfur is in Period 3, its valence shell has 3*s*, 3*p*, and 3*d* subshells, which together can accommodate more than eight electrons. Therefore, sulfur is able to form more than four bonds, so we are allowed to increase the bond order in the S—O bonds by moving electron pairs to create sulfur–oxygen double bonds as follows:



(Structure II)

Now we have a Lewis structure that better fits experimental observations because the sulfur–oxygen double bonds are expected to be shorter than the sulfur–oxygen single bonds. Because this second Lewis structure agrees better with the actual structure of the molecule, it is the *preferred* Lewis structure, even though it violates the octet rule.

Assigning Formal Charges to Atoms

Are there any criteria that we could have applied that would have allowed us to predict that the second Lewis structure for H_2SO_4 is better than the one with only single bonds, even though it seems to violate the octet rule unnecessarily? To answer this question, let's take a closer look at the two Lewis structures we've drawn.

In Structure I, there are only single bonds between the sulfur and oxygen atoms. If the electrons in the bonds are shared equally by S and O, then each atom "owns" half of the electron pair, or the equivalent of one electron. In other words, the four single bonds place the equivalent of four electrons in the valence shell of the sulfur. An isolated single atom of sulfur, however, has six valence electrons, so in Structure I the sulfur appears to have two electrons *less* than it does as just an isolated atom. Thus, at least in a *bookkeeping* sense, it would appear that if sulfur obeyed the octet rule in H_2SO_4, it would have a charge of 2+. This *apparent* charge on the sulfur atom is called its **formal charge.**

Notice that in defining formal charge, we've stressed the word "apparent." *The formal charge arises because of the bookkeeping we've done and should not be confused with whatever the actual charge is on an atom in the molecule.* (The situation is somewhat similar to the oxidation numbers you learned to assign in Chapter 6, which are artificial charges assigned according to a set of rules.) Here's how formal charges are assigned.

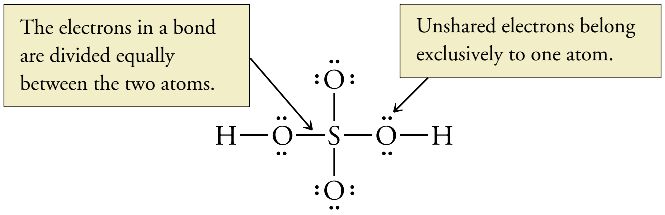
■ The actual charges on the atoms in a molecule are determined by the relative electronegativities of the atoms.

Calculating the Formal Charge on Atoms in a Lewis Structure

1. For each atom, write down the number of valence electrons in an isolated atom of the element.
2. Using the Lewis structure, add up the valence electrons that "belong to" the atom in the molecule or ion, and then subtract this total from the value in Step 1. The result is the formal charge on the atom.
3. The sum of the formal charges in a structure must equal the charge on the particle.

Calculating formal charges

In performing the calculation in Step 2, electrons in bonds are divided equally between the two atoms, while unshared electrons are assigned exclusively to the atom on which they reside. For example, for Structure I above, we have



The electrons in a bond are divided equally between the two atoms.

Unshared electrons belong exclusively to one atom.

Therefore, the calculation of formal charge is summarized by the following equation:

$$\boxed{\text{formal charge} = \left(\begin{array}{c}\text{number of } e^- \text{ in valence}\\ \text{shell of the isolated atom}\end{array}\right) - \overbrace{\left(\begin{array}{c}\text{number of bonds}\\ \text{to the atom}\end{array} + \begin{array}{c}\text{number of}\\ \text{unshared } e^-\end{array}\right)}^{\begin{array}{c}\text{Calculated number of electrons in the valence}\\ \text{shell of the atom in the Lewis structure}\end{array}}} \qquad \textbf{(9.3)}$$

For example, for the sulfur in Structure I, we get

There are 4 bonds to the sulfur atom.

$$\text{formal charge on S} = 6 - (4 + 0) = +2$$

An isolated S atom has 6 electrons.

There are no unshared pairs on the sulfur.

Let's also calculate the formal charges on the hydrogen and oxygen atoms in Structure I. An isolated H atom has one electron. In Structure I each H has one bond and no unshared electrons. Therefore,

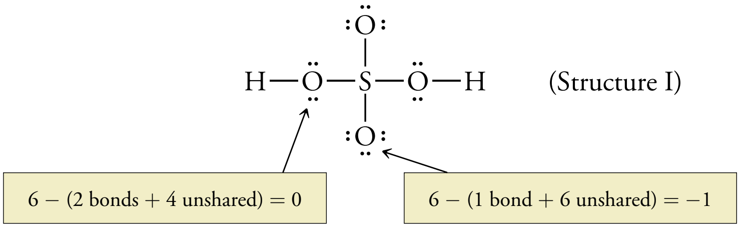
$$\text{formal charge on H} = 1 - (1 + 0) = 0$$

In Structure I, we also see that there are two kinds of oxygen to consider. An isolated oxygen atom has six electrons, so we have, for the oxygens also bonded to hydrogen,

$$\text{formal charge} = 6 - (2 + 4) = 0$$

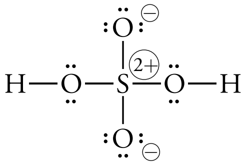
and for the oxygens not bonded to hydrogen,

$$\text{formal charge} = 6 - (1 + 6) = -1$$


6 − (2 bonds + 4 unshared) = 0
6 − (1 bond + 6 unshared) = −1

(Structure I)

Nonzero formal charges are indicated in a Lewis structure by placing them in circles alongside the atoms, as follows:



Notice that the sum of the formal charges in the molecule adds up to zero. *After you've assigned formal charges, it is important to always check that the sum of the formal charges in the Lewis structure adds up to the charge on the particle.*

Now let's look at the formal charges in Structure II. For sulfur we have

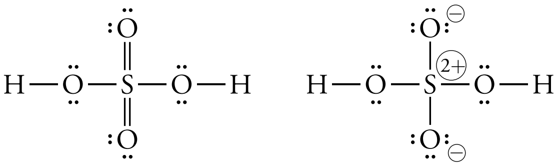
$$\text{formal charge on S} = 6 - (6 + 0) = 0$$

so the sulfur has no formal charge. The hydrogens and the oxygens that are also bonded to H are the same in this structure as before, so they have no formal charges. And finally, the oxygens that are not bonded to hydrogen have

$$\text{formal charge} = 6 - (2 + 4) = 0$$

These oxygens also have no formal charges.

Now let's compare the two structures side by side.



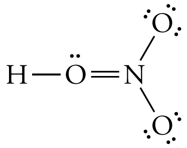
Imagine changing the one with the double bonds (no formal charges on any atoms) to the one with the single bonds (having two negative and two positive charges). In doing so, we've create two pairs of positive–negative charge from something electrically neutral. Because the process involves separating negative charges from positive charges, it would produce an increase in the potential energy. Our conclusion, therefore, is that the singly bonded structure on the right has a higher potential energy than the one with the double bonds. In general, the lower the potential energy of a molecule, the more stable it is. Therefore, the lower energy structure with the double bonds is, in principle, the more stable structure, so it is preferred over the one with only single bonds. This now gives us a rule that we can use in selecting the best Lewis structures for a molecule or ion:

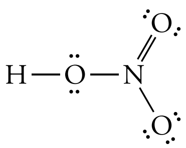
Selecting the best Lewis structure

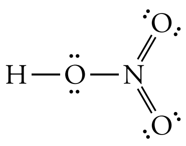
> When several Lewis structures are possible, the one with formal charges closest to zero is the most stable and is preferred.

Example 9.9
Selecting Lewis Structures Based on Formal Charges

A student drew the following three Lewis structures for the nitric acid molecule:


(I)


(II)


(III)

Which one is preferred?

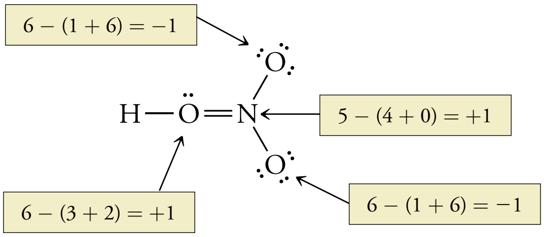
Analysis: When we have to select among several Lewis structures to find the best one, we first have to assign formal charges to each of the atoms. As a rule, the structure with the formal charges closest to zero will be the best structure. We have to be careful, however, that we don't select a structure in which an atom is assigned more electrons than its valence shell can actually hold. Such a structure must be eliminated from consideration.

Assembling the Tools: To assign the formal charges, the tool we use is Equation 9.3 on page 389.

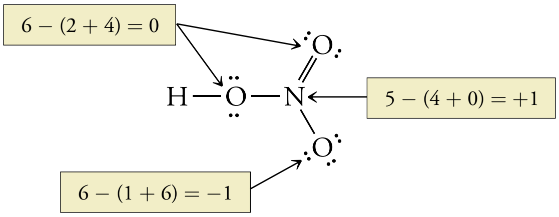
Solution: Except for hydrogen, all of the atoms in the molecule are from Period 2, and therefore can have a maximum of eight electrons in their valence shells. (Period 2 elements *never* exceed an octet because their valence shells have only *s* and *p* subshells and can accommodate a maximum of eight electrons.) Scanning the structures, we see that I and II show octets around both N and O. However, the nitrogen in Structure III has 5 bonds to it, which require 10 electrons. Therefore, this structure is not acceptable and can be eliminated immediately. Our choice is then between Structures I and II. Let's calculate formal charges on the atoms in each of them.

■ In Structure III, the formal charges are zero on each of the atoms, but this cannot be the "preferred structure" because the nitrogen atom has too many electrons in its valence shell.

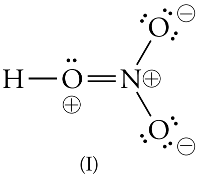
Structure I:

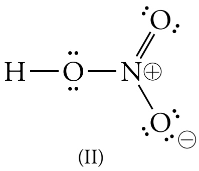


Structure II:



Next, we place the formal charges on the atoms in the structures.


(I)

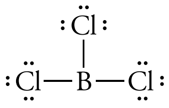

(II)

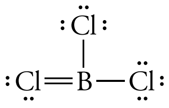
Because Structure II has fewer formal charges than Structure I, it is the lower-energy, preferred Lewis structure for HNO_3.

■ **Is the Answer Reasonable?** One simple check we can do is to add up the formal charges in each structure. The sum must equal the net charge on the particle, which is zero for HNO_3. Adding formal charges gives zero for each structure, so we can be confident we've assigned them correctly. This gives us confidence in our answer, too.

Example 9.10
Selecting Lewis Structures Based on Formal Charges

The following two structures can be drawn for BCl_3:


(I)

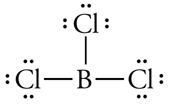

(II)

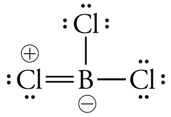
Why is the one that violates the octet rule preferred?

■ **Analysis:** We're asked to select between Lewis structures, which tells us that we have to consider formal charges. We'll assign them and then see whether we can answer the question.

■ **Assembling the Tools:** To assign formal charges we use Equation 9.3.

■ **Solution:** Assigning formal charges gives

(I)


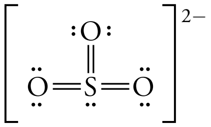
(II)


In Structure I all the formal charges are zero. In Structure II, two of the atoms have formal charges, so this alone would argue in favor of Structure I. There is another argument in favor as well. Notice that the formal charges in Structure II place the positive charge on the more electronegative chlorine atom and the negative charge on the less electronegative boron. If charges could form in this molecule, they certainly would not be expected to form in this way. Therefore, there are two factors that make the structure with the double bond unfavorable, so we usually write the Lewis structure for BCl_3 as shown in (I).

■ **Is the Answer Reasonable?** We've assigned the formal charges correctly, and our reasoning seems sound, so we appear to have answered the question adequately.

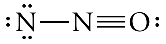
Practice Exercises

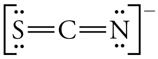
9.16 | A student drew the following Lewis structure for the sulfite ion, SO_3^{2-}:



Is this the best Lewis structure for the ion? (*Hint:* Negative formal charges should be on the more electronegative atoms.)

9.17 | Assign formal charges to the atoms in the following Lewis structures:

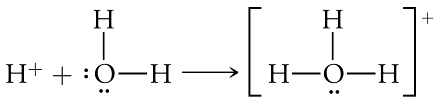
(a)

$:\ddot{N}-N\equiv O:$

(b)

$[\ddot{S}=C=\ddot{N}]^-$

9.18 | Select the preferred Lewis structure for (a) SO_2, (b) $HClO_3$, and (c) H_3PO_4.

Coordinate Covalent Bonds

Often we use Lewis structures to follow the course of chemical reactions. For example, we can diagram how a hydrogen ion combines with a water molecule to form the hydronium ion, a process that occurs in aqueous solutions of acids.



The formation of the bond between H^+ and H_2O follows a different path than the covalent bonds we discussed earlier in this chapter. For instance, when two H atoms combine to form H_2, each atom brings one electron to the bond.

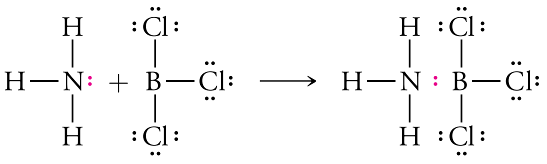
$$H\cdot + \cdot H \longrightarrow H{-}H$$

But in the formation of H_3O^+, both of the electrons that become shared between the H^+ and the O originate on the oxygen atom of the water molecule. *This type of bond, in which both electrons of the shared pair come from just one of the two atoms, is called a* **coordinate covalent bond.**

Although we can make a distinction about the origin of the electrons shared in the bond, once the bond is formed a coordinate covalent bond is really the same as any other covalent bond. In other words, we can't tell where the electrons in the bond came from *after* the bond has been formed. In the H_3O^+ ion, for example, all three O—H bonds are identical once they've been formed.

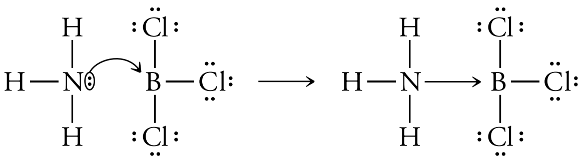
The concept of a coordinate covalent bond is helpful in explaining what happens to atoms in a chemical reaction. For example, when ammonia is mixed with boron trichloride, an exothermic reaction takes place and the compound NH_3BCl_3 is formed in which there is a boron–nitrogen bond. Using Lewis structures, we can diagram this reaction as follows.

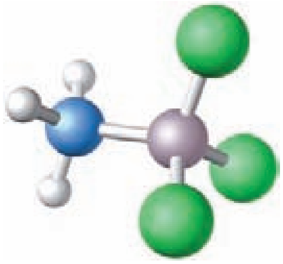
■ All electrons are alike. We are using different colors for them so we can see where the electrons in the bond came from.



In the reaction, we might say that "the boron forms a coordinate covalent bond with the nitrogen of the ammonia molecule."

An arrow sometimes is used to represent the donated pair of electrons in a coordinate covalent bond. The direction of the arrow indicates the direction in which the electron pair is donated, in this case from the nitrogen to the boron.





The addition compound formed from ammonia and boron trichloride. The light blue colored atom is boron.

Compounds like BCl_3NH_3, which are formed by simply joining two smaller molecules, are sometimes called **addition compounds.**

Practice Exercises

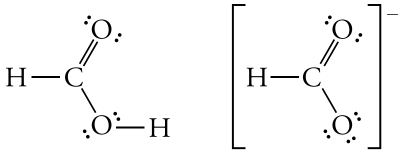
9.19 | Use Lewis structures to show how the formation of NH_4^+ from NH_3 and H^+ involves formation of a coordinate covalent bond. How does this bond differ from the other N—H bonds in NH_4^+? (*Hint:* Keep in mind the definition of a coordinate covalent bond.)

9.20 | Use Lewis structures to explain how the reaction between hydroxide ion and hydrogen ion involves the formation of a coordinate covalent bond.

9.9 | Resonance Structures

■ The IUPAC name for formic acid is methanoic acid and the formate ion is the methanoate ion.

There are some molecules and ions for which we cannot write Lewis structures that agree with experimental measurements of bond length and bond energy. An example is the formate ion, CHO_2^-, formed by neutralizing formic acid, $HCHO_2$. Following the usual steps, we would write the Lewis structure of the formate ion as shown on the right below.

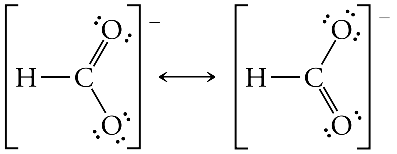


formic acid   formate ion

Formic acid is the substance that causes the stinging sensation in bites from fire ants. *(WildPicture/Alamy)*

This structure suggests that in the CHO_2^- ion, one carbon–oxygen bond should be longer than the other, but experiments show that the C—O bond lengths are identical, with lengths that are about halfway between the expected values for a single bond and a double bond. The Lewis structure doesn't match the experimental evidence, and there's no way to write one that does. It would require showing all of the electrons in pairs and, at the same time, showing 1.5 pairs of electrons in each carbon–oxygen bond.

The way we get around problems like this is through the use of a concept called **resonance.** We view the actual structure of the molecule or ion, which we cannot draw satisfactorily, as a composite, or average, of a number of Lewis structures that we can draw. For example, for formate ion we write



■ It is important to understand that when we draw resonance structures *no atoms are moved*; the electrons are just redistributed.

where we have simply shifted electrons around in going from one structure to the other. The bond between the carbon and a particular oxygen is depicted as a single bond in one structure and as a double bond in the other. The average of these is 1.5 bonds (halfway between a single and a double bond), which is in agreement with the experimental bond lengths. These two Lewis structures are called **resonance structures** or **contributing structures.** The actual structure of the ion, which we can't draw, is called a **resonance hybrid** of these two resonance structures. The double-ended arrow is used to show that we are drawing resonance structures and implies that the true hybrid structure is a composite of the two resonance structures.

A zonkey is the hybrid offspring of a zebra and a donkey. It has characteristics of both of its parents, but is never exactly like either one of them. It certainly isn't a zebra one minute and a donkey the next! *(JIJIPRESS/AFP/Getty Images, Inc.)*

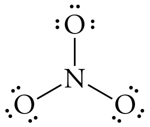
Some students find the term *resonance* somewhat misleading. The word itself suggests that the actual structure flip-flops back and forth between the two structures shown. This is *not* the case! We are simply using structures that we are able to draw to describe an actual structure that we cannot draw. It's a bit like trying to imagine what a *zonkey* looks like by viewing photos of a zebra and a donkey. Although a zonkey may have characteristics of both parents, a zonkey is a zonkey; it doesn't flip back and forth between being a zebra one minute and a donkey the next. Similarly, a *resonance hybrid* also has characteristics of its "parents," but it doesn't flip back and forth between the contributing structures.

When We Draw Resonance Structures

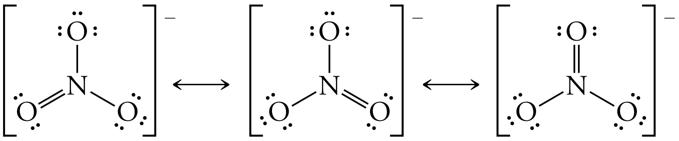
TOOLS

Determining resonance structures

There is a simple way to determine when resonance should be applied to Lewis structures. If you find that you must move electrons to create one or more double bonds while following the procedures developed earlier, the number of resonance structures is equal to the number of equivalent choices for the locations of the double bonds. For example, in drawing the Lewis structure for the NO_3^- ion, we reach the stage



A double bond must be created to give the nitrogen an octet. Since it can be placed in any one of three locations, there are three resonance structures for this ion.



■ The three oxygens in NO_3^- are said to be equivalent; that is, they are all alike in their chemical environment. Each oxygen is bonded to a nitrogen atom that's attached to two other oxygen atoms.

Notice that each structure is the same, except for the location of the double bond.

In the nitrate ion, the extra bond that appears to "move around" from one structure to another is actually divided among all three bond locations. Therefore, the **average bond order** in the N—O bonds is expected to be $1\frac{1}{3}$, or 1.33. In general, we can calculate the average bond order by adding up the total number of bonds and dividing by the number of equivalent positions. In the NO_3^- ion, we have a total of *four* bonds (two single bonds and a double bond) distributed over *three* equivalent positions, so the bond order is $4/3 = 1\frac{1}{3}$.

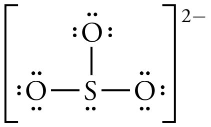
TOOLS

Calculating average bond orders

Example 9.11
Drawing Resonance Structures

Use formal charges to show that resonance applies to the preferred Lewis structure for the sulfite ion, SO_3^{2-}. Draw the resonance structures and determine the average bond order of the S—O bonds.

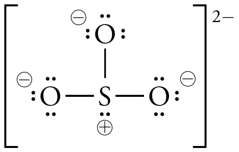
■ **Analysis:** Following our usual procedure we obtain the following Lewis structure:



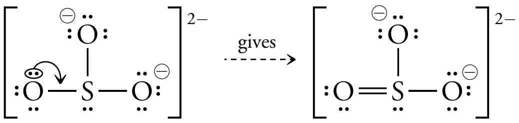
All of the valence electrons have been placed into the structure and we have octets around all of the atoms, so it doesn't seem that we need the concept of resonance. However, the question refers to the "preferred" structure, which suggests that we are going to have to assign formal charges and determine what the preferred structure is. Then we can decide whether the concept of resonance will apply.

■ **Assembling the Tools:** To assign formal charges, our tool is Equation 9.3. If a double bond occurs in the preferred structure, the number of equivalent positions equals the number of resonance structures. The average bond order will be calculated from the number of bonds distributed over the three equivalent bond locations.

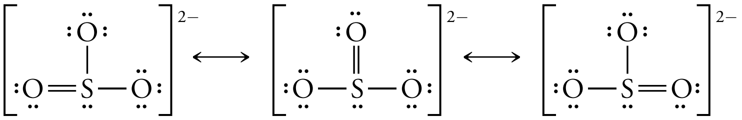
■ **Solution:** When we assign formal charges, we get



We can obtain a better Lewis structure if we can reduce the number of formal charges. This can be accomplished by moving an unshared electron pair from one of the oxygens into an S—O bond, thereby forming a double bond. Let's do this using the oxygen at the left.



However, we could have done this with any of the three S—O bonds, so there are three equivalent choices for the location of the double bond. Therefore, there are three resonance structures.

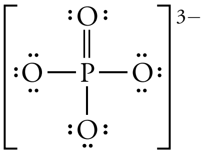


As with the nitrate ion, we expect an average bond order of 1.33.

■ **Is the Answer Reasonable?** If we can answer "yes" to the following questions, the problem is solved correctly: Have we counted valence electrons correctly? Have we properly placed the electrons into the skeletal structure? Do the formal charges we've calculated add up to the charge on the SO_3^{2-} ion? Have we correctly determined the number of equivalent positions for the double bond? Have we computed the average bond order correctly? All the answers are "yes", so we have solved the problem correctly.

Practice Exercises

9.21 | The phosphate ion has the following Lewis structure, where we've used formal charges to obtain the best structure.



How many resonance structures are there for this ion? (*Hint:* How many equivalent positions are there for the double bond?)

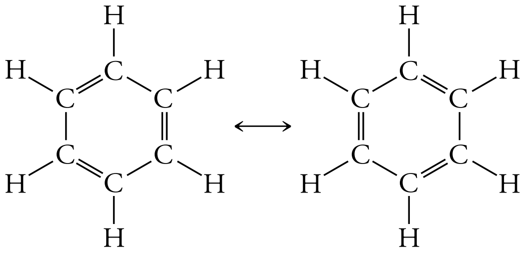
9.22 | Draw the resonance structures for HCO_3^-.

9.23 | Determine the preferred Lewis structure for the bromate ion, BrO_3^-, and, if appropriate, draw resonance structures.

Stability of Molecules with Resonance Structures

One of the benefits that a molecule or ion derives from existing as a resonance hybrid is that its total energy is lower than that of any one of its contributing structures. A particularly important example of this occurs with the compound benzene, C_6H_6. This is a flat hexagonal ring-shaped molecule (Figure 9.14) with a basic structure that appears in many important organic molecules, ranging from plastics to amino acids.

Two resonance structures are usually drawn for benzene.



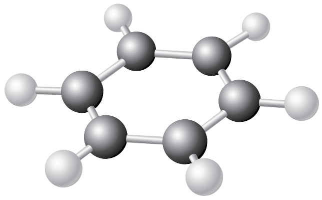
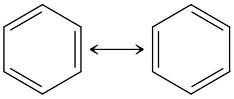
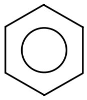


Figure 9.14 | **Benzene.** The molecule has a planar hexagonal structure.

These are generally represented as hexagons with dashes showing the locations of the double bonds. It is assumed that at each apex of the hexagon there is a carbon bonded to a hydrogen as well as to the adjacent carbon atoms.



Usually, the actual structure of benzene (that of its resonance hybrid) is represented as a hexagon with a circle in the center. This is intended to show that the electron density of the three extra bonds is evenly distributed around the ring.



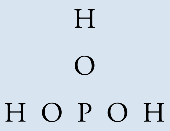
This is the way the structure of benzene is usually represented

Although the individual resonance structures for benzene show double bonds, the molecule does not react like other organic molecules that have true carbon–carbon double bonds. The reason appears to be that the resonance hybrid is considerably more stable than either of the resonance forms. In fact, it has been calculated that the actual structure of the benzene molecule is more stable than either of its resonance structures by approximately 146 kJ/mol. This extra stability achieved through resonance is called the **resonance energy.**

Analyzing and Solving Multi-Concept Problems

Phosphorous acid has the formula H_3PO_3. It was found that a sample of the acid weighing 0.3066 g was neutralized completely by 0.4196 g of KOH. Use these data to write the preferred Lewis structure for H_3PO_3.

Analysis At first, it seems like we should be able to follow the guidelines developed earlier in this chapter to arrive at the Lewis structure. For example, on page 384 you learned that for oxoacids, the hydrogens that can be released as H^+ are bonded to oxygen, which in turn is bonded to the central atom of the oxoacid. The formula H_3PO_3 suggests a triprotic acid, which would have the following skeletal structure.



$$\begin{matrix} & & H & & \\ & & O & & \\ H & O & P & O & H \end{matrix}$$

We can use the data presented for the neutralization of the acid by KOH to confirm whether or not this is the correct arrangement of atoms.

From the neutralization data we can calculate the number of moles of KOH required to neutralize one mole of the acid. This will tell us the number of "acidic" hydrogens in a molecule of the acid. If the acid is indeed a triprotic acid as indicated by the skeletal structure above, three moles of KOH should be needed to neutralize one mole of acid.

If the stoichiometry of the neutralization reaction tells us the acid is triprotic, we can then proceed to add the necessary number of electrons to the skeletal structure above. However, if the neutralization reaction tells us H_3PO_3 is not triprotic, then we have to refine the skeletal structure before proceeding further. Here, then, is our strategy.

Part 1: Use the neutralization data to determine the number of moles of KOH that reacts with 1.00 mol of H_3PO_3.

Part 2: Refine the skeletal structure, if necessary, to make it conform to the results of the computation in Part 1.

Part 3: Add the necessary number of electrons to obtain the compete Lewis structure. Then reduce formal charges, if possible, to obtain the preferred structure.

PART 1

Assembling the Tools The data we need to perform the calculation are the molar masses of H_3PO_3 (81.994 g mol^{-1}) and KOH (56.108 g mol^{-1}). From the data in the problem, we can also set up the equivalence

$$0.3066\text{ g H}_3\text{PO}_3 \Leftrightarrow 0.4196\text{ g of KOH}$$

Solution This part of the problem can be expressed as

$$1\text{ mol H}_3\text{PO}_3 \Leftrightarrow ?\text{ mol KOH}$$

Using dimensional analysis gives us.

$$1\ \cancel{\text{mol H}_3\text{PO}_3} \times \frac{81.994\ \cancel{\text{g H}_3\text{PO}_3}}{1\ \cancel{\text{mol H}_3\text{PO}_3}} \times \frac{0.4196\ \cancel{\text{g KOH}}}{0.3066\ \cancel{\text{g H}_3\text{PO}_3}} \times \frac{1\text{ mol KOH}}{56.108\ \cancel{\text{g KOH}}} = 2.00\text{ mol KOH}$$

Because only 2 moles of KOH are needed to neutralize 1 mole of the acid, the acid must be diprotic. We are going to have to make changes in the skeletal structure to reflect this.

PART 2

Assembling the Tools We need to use the general guidelines for constructing skeletal structures, modified as necessary to make the structure conform to the results of Part 1.

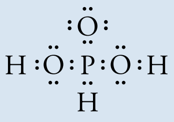
Solution On page 384 you learned that acidic hydrogens in an oxoacid are bonded to oxygen atoms, which are bonded in turn to the central atom. Because H_3PO_3 is diprotic, only two such hydrogens are present. So what about the third hydrogen? If it's not bonded to oxygen, then it must be bonded to the phosphorus atom. This suggests the skeletal structure:

O
H O P O H
H

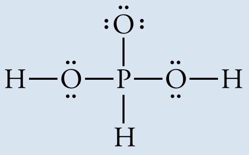
PART 3

Assembling the Tools Our tool is the procedure for drawing Lewis structures given on page 383. We will also use formal charges (page 389) to determine whether we have the preferred structure.

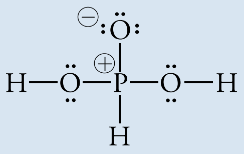
Solution Phosphorus (Group 5A) contributes 5 electrons; each oxygen (Group 6A) contributes 6 electrons, and each hydrogen contributes one electron. The total is 26e^-. Following the usual procedure, the Lewis structure is



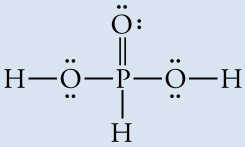
or



Assigning formal charges gives us



We can reduce the formal charges by moving a lone electron pair from the oxygen at the top into the phosphorus–oxygen bond, giving a double bond.



$$\mathrm{H{-}\underset{\cdot\cdot}{\ddot{O}}{-}\overset{\overset{\ddot{O}:}{\|}}{\underset{\underset{H}{|}}{P}}{-}\underset{\cdot\cdot}{\ddot{O}}{-}H}$$

This structure has no formal charges and is the preferred structure of the molecule.

■ **Is the Answer Reasonable?** The fact that the stoichiometry calculation gives a whole number of moles of KOH per mole of H_3PO_3 suggests this part of the problem has been solved correctly. Dimensional analysis also gives the correct units, so we can conclude the calculation is correct. The alternative skeletal structure agrees with the stoichiometry, so it is reasonable. Finally, we can check to be sure we've supplied the correct number of electrons, which we have, so our Lewis structure appears to be reasonable.

Summary

Ionic Bonding. In ionic compounds, the forces of attraction between positive and negative ions are called **ionic bonds.** The formation of ionic compounds by electron transfer is favored when atoms of low ionization energy react with atoms of high electron affinity. The chief stabilizing influence in the formation of ionic compounds is the release of the **lattice energy.** When atoms of the elements in Groups 1A and 2A as well as the nonmetals form ions, they usually gain or lose enough electrons to achieve a noble gas electron configuration. Transition elements lose their outer *s* electrons first, followed by loss of *d* electrons from the shell below the outer shell. Post-transition metals lose electrons from their outer *p* subshell first, followed by electrons from the outer *s* subshell.

Covalent Bonding. Electron sharing between atoms occurs when electron transfer is energetically too "expensive." Shared electrons attract the positive nuclei, and this leads to a lowering of the potential energy of the atoms as a covalent bond forms. Electrons generally become paired when they are shared. An atom tends to share enough electrons to complete its valence shell. Except for hydrogen, the valence shell usually holds eight electrons, which forms the basis of the octet rule. The **octet rule** states that atoms of the representative elements tend to acquire eight electrons in their outer shells when they form bonds. **Single, double,** and **triple bonds** involve the sharing of one, two, and three pairs of electrons, respectively, between two atoms. Boron and beryllium often have less than an octet in their compounds. Atoms of the elements of Period 2 cannot have more than an octet because their outer shells can hold only eight electrons. Elements in Periods 3, 4, 5, and 6 can exceed an octet if they form more than four bonds.

Bond energy (the energy needed to separate the bonded atoms) and **bond length** (the distance between the nuclei of the atoms connected by the bond) are two experimentally measurable quantities that can be related to the number of pairs of electrons in the bond. For bonds between atoms of the same elements, bond energy increases and bond length decreases as the bond order increases.

Electronegativity and Polar Bonds. The attraction an atom has for the electrons in a bond is called the atom's **electronegativity.** When atoms of different electronegativities form a bond, the electrons are shared unequally and the bond is **polar,** with **partial positive** and **partial negative** charges at opposite ends. This causes the bond to be an electric **dipole.** In a **polar molecule,** such as HCl, the product of the charge at either end multiplied by the distance between the charges gives the **dipole moment,** μ. When the two atoms have the same electronegativity, the bond is **nonpolar.** The extent of polarity of the bond depends on the electronegativity difference between the two bonded atoms. When the electronegativity difference is very large, ionic bonding results. A bond is approximately 50% ionic when the electronegativity difference is 1.7. In the periodic table, electronegativity increases from left to right across a period and from bottom to top in a group.

Reactivity and Electronegativity. The **reactivity** of metals is related to the ease with which they are oxidized (lose electrons); for nonmetals it is related to the ease with which they are reduced (gain electrons). Metals with low electronegativities lose electrons easily, are good reducing agents, and tend to be very reactive. The most reactive metals are located in Groups 1A and 2A, and their ease of oxidation increases going down the group. For nonmetals, the higher the electronegativity, the stronger is their ability to serve as oxidizing agents. In **displacement reactions,** a more electronegative nonmetal is often able to displace one of lower electronegativity from its compounds. The strongest oxidizing agent is fluorine. Among the halogens, oxidizing strength decreases from fluorine to iodine.

Lewis Symbols and Lewis Structures. Lewis symbols are a bookkeeping device used to keep track of valence electrons in ionic and covalent bonds. The **Lewis symbol** of an element consists of the element's chemical symbol surrounded by a number of dots equal to the number of valence electrons. In the **Lewis structure** for an ionic compound, the Lewis symbol for the anion is enclosed in brackets (with the charge written outside) to show that all the electrons belong entirely to the ion. The Lewis structure for a molecule or polyatomic ion uses pairs of dots between chemical symbols to represent shared pairs of electrons. The electron pairs in covalent bonds usually are represented by dashes; one dash equals two electrons. The following procedure is used to draw the Lewis structure: (1) decide on the **skeletal structure** (remember that the least electronegative atom is usually the central atom and is usually first in the formula); (2) count all the valence electrons, taking into account the charge, if any; (3) place a pair of electrons in each bond; (4) complete the octets of atoms other than the central atom (but remember that hydrogen can only have two electrons); (5) place any left-over electrons on the central atom in pairs; (6) if the central atom still has less than an octet, move electron pairs to make double or triple bonds.

Formal Charges. The **formal charge** assigned to an atom in a Lewis structure (which usually differs from the actual charge on the atom) is calculated as the difference between the number of valence electrons of an isolated atom of the element and the number of electrons that "belong" to the atom because of its bonds to other atoms and its unshared valence electrons. The sum of the formal charges always equals the net charge on the molecule or ion. The most stable (lowest energy) Lewis structure for a molecule or ion is the one with formal charges closest to zero. This is usually the preferred Lewis structure for the particle.

Coordinate Covalent Bonding. For bookkeeping purposes, we sometimes single out a covalent bond whose electron pair originated from one of the two bonded atoms. An arrow is sometimes used to indicate the donated pair of electrons. Once formed, a coordinate covalent bond is no different from any other covalent bond.

Resonance. Two or more atoms in a molecule or polyatomic ion are *chemically equivalent* if they are attached to the same kinds of atoms or groups of atoms. Bonds to chemically equivalent atoms must be the same; they must have the same bond length and the same bond energy, which means they must involve the sharing of the same number of electron pairs. Sometimes the Lewis structures we draw suggest that the bonds to chemically equivalent atoms are not the same. Typically, this occurs when it is necessary to form multiple bonds during the drawing of a Lewis structure. When alternatives exist for the location of a multiple bond among two or more equivalent atoms, then each possible Lewis structure is actually a **resonance structure** or **contributing structure,** and we draw them all. In drawing resonance structures, the relative locations of the nuclei must be identical in all. The **average bond order** is calculated from the total number of bonds distributed over the equivalent bond locations. Remember that none of the resonance structures corresponds to a real molecule, but their composite—the **resonance hybrid**—does approximate the actual structure of the molecule or ion.

TOOLS Tools for Problem Solving

In this chapter you learned to apply the following concepts as tools in solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

Electron configurations of ions of the representative elements (page 363)

Metals in Groups 1A and 2A, aluminum, and the nonmetals obey the octet rule when they form ions. This knowledge is helpful when you have to write the electron configurations of ions of these elements.

Order in which electrons are lost from an atom (page 363)

Electrons are lost first from the shell with largest n. For a given shell, electrons are lost from subshells in the following order: f before d before p before s. Use this knowledge to obtain electron configurations of ions of the transition and post-transition metals.

Lewis symbols (page 366)

Lewis symbols are a bookkeeping device that we use to keep track of valence electrons in atoms and ions. For a neutral atom of the representative elements, the Lewis symbol consists of the atomic symbol surrounded by dots equal in number to the group number.

Octet rule and covalent bonding (page 371)

The octet rule helps us construct Lewis structures for covalently bonded molecules. Elements in Period 2 never exceed an octet in their valence shells.

Dipole moment (page 378)
Dipole moments are a measure of the polarity of molecules, so they can be used to compare molecular polarity. The dipole moment (μ) of a diatomic molecule is calculated as the charge on an end of the molecule, q, multiplied by the bond length, r. Dipole moments are expressed in debye units.

$$\mu = q \times r$$

Periodic trends in electronegativity (page 381)
The trends revealed in Figure 9.9 allow us to use the locations of elements in the periodic table to estimate the degree of polarity of bonds and to estimate which of two atoms in a bond is the most electronegative.

Trends in the reactivity of metals in the periodic table (page 381)
A knowledge of where the most reactive and least reactive metals are located in the periodic table gives a qualitative feel for how reactive a metal is.

Trends in the reactivity of nonmetals in the periodic table (page 382)
The periodic table correlates the position of a nonmetal with its strength as an oxidizing agent. Oxidizing ability increases from left to right across a period and from bottom to top in a group.

Method for drawing Lewis structures (page 383)
The method described in Figure 9.12 yields Lewis structures in which the maximum number of atoms obey the octet rule.

Correlation between bond properties and bond order (page 388)
The correlations allow us to compare experimental covalent bond properties (bond energy and bond length) with those predicted by theory.

Method for calculating formal charges (page 389)
Use formal charges to select the best Lewis structure for a molecule or polyatomic ion. The best structure is usually the one with the fewest formal charges. Assign formal charges to atoms as follows:

$$\text{Formal charge} = \begin{bmatrix}\text{number of } e^- \text{ in valence} \\ \text{shell of the isolated atom}\end{bmatrix} - \begin{bmatrix}\text{number of bonds} \\ \text{to the atom}\end{matrix} + \begin{matrix}\text{number of} \\ \text{unshared } e^-\end{bmatrix}$$

Selecting the best Lewis structure (page 390)
The structure having the smallest formal charges is preferred. Be sure none of the atoms in the structure appears to have more electrons than permitted by its location in the periodic table.

Determining resonance structures (page 394)
Expect resonance structures when there is more than one option for assigning the location of a double bond. Determine the number of equivalent positions for the double bond. That number is the number of resonance structures you should draw.

Calculating average bond order (page 395)
To calculate the average bond order for resonance structures, add up the total number of bonds and divide by the number of equivalent positions in which they are drawn.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Ionic Bonding

9.1 What must be true about the change in the total potential energy of a collection of atoms for a stable compound to be formed from the elements?

9.2 What is an *ionic bond?*

9.3 How is the tendency to form ionic bonds related to the IE and EA of the atoms involved?

9.4 Define the term *lattice energy*. In what ways does the lattice energy contribute to the stability of ionic compounds?

9.5 Magnesium forms compounds containing the ion Mg^{2+} but not the ion Mg^{3+}. Why?

9.6 Why doesn't chlorine form the ion Cl^{2-} in compounds?

9.7 Why do many of the transition elements in Period 4 form ions with a 2+ charge?

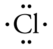
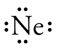
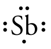
9.8 If we were to compare the first, second, third, and fourth ionization energies of aluminum, between which pair of successive ionization energies would there be the largest difference? (Refer to the periodic table when answering this question.)

9.9 In each of the following pairs of compounds, which would have the larger lattice energy: **(a)** CaO or Al_2O_3, **(b)** BeO or SrO, **(c)** NaCl or NaBr?

Lewis Symbols

9.10 The Lewis symbol for an atom only accounts for electrons in the valence shell of the atom. Why are we not concerned with the other electrons?

9.11 Which of these Lewis symbols is incorrect?

(a) **(b)**  **(c)**  **(d)** 

Electron Sharing

9.12 In terms of the potential energy change, why doesn't ionic bonding occur when two nonmetals react with each other?

9.13 Describe what happens to the electron density around two hydrogen atoms as they come together to form an H_2 molecule.

9.14 What happens to the energy of two hydrogen atoms as they approach each other? What happens to the spins of the electrons?

9.15 Is the formation of a covalent bond endothermic or exothermic?

9.16 What factors control the bond length in a covalent bond?

Covalent Bonding and the Octet Rule

9.17 What is the *octet rule*? What is responsible for it?

9.18 How many covalent bonds are normally formed by **(a)** hydrogen, **(b)** carbon, **(c)** oxygen, **(d)** nitrogen, and **(e)** chlorine?

9.19 Why do Period 2 elements never form more than four covalent bonds? Why are Period 3 elements able to exceed an octet?

9.20 Define **(a)** *single bond,* **(b)** *double bond,* and **(c)** *triple bond.*

9.21 The Lewis structure for hydrogen cyanide is $H{-}C{\equiv}N{:}$. Draw circles enclosing electrons to show that carbon and nitrogen obey the octet rule.

9.22 Why doesn't hydrogen obey the octet rule?

Compounds of Carbon

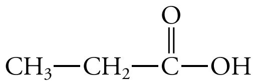
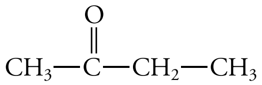
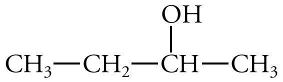
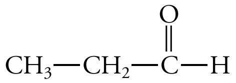
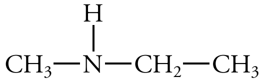
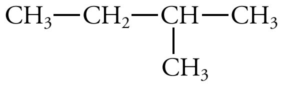
9.23 Sketch the Lewis structures for **(a)** methane, **(b)** ethane, and **(c)** propane.

9.24 Draw the structure for a hydrocarbon that has a chain of six carbon atoms linked by single bonds. How many hydrogen atoms does the molecule have? What is the molecular formula for the compound?

9.25 How many *different* molecules have the formula C_5H_{12}? Sketch their structures.

9.26 What is a carbonyl group? In which classes of organic molecules that we've studied do we find a carbonyl group?

9.27 Match the compounds on the left with the family types on the right.

 $CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$	hydrocarbon
 $CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3$	aldehyde
 $CH_3{-}CH_2{-}\overset{\overset{\displaystyle OH}{\|}}{CH}{-}CH_3$	amine
 $CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$	acid
 $CH_3{-}\overset{\overset{\displaystyle H}{\|}}{N}{-}CH_2{-}CH_3$	alcohol
 $CH_3{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{\|}}{CH}{-}CH_3$	ketone

9.28 Write a chemical equation for the ionization in water of the acid in Question 9.27. Is the acid strong or weak? Draw the Lewis structure for the ion formed by the acid when it ionizes.

9.29 Write a chemical equation for the reaction of the amine in Question 9.27 with water. Draw the Lewis structure for the ion formed by the amine.

9.30 Write the net ionic equation for the aqueous reaction of the acid and amine in Question 9.27 with each other. (Use molecular formulas.)

9.31 Draw the structures of **(a)** ethylene and **(b)** acetylene.

Polar Bonds and Electronegativity

9.32 What is a polar covalent bond?

9.33 Define *dipole moment* in the form of an equation. What is the value of the *debye* (with appropriate units)?

9.34 Define electronegativity. On what basis did Pauling develop his scale of electronegativities?

9.35 Which element has the highest electronegativity? Which is the second most electronegative element?

9.36 Among the following bonds, which are more ionic than covalent? **(a)** Si—O, **(b)** Ba—O, **(c)** Se—Cl, **(d)** K—Br

9.37 If an element has a low electronegativity, is it likely to be classified as a metal or a nonmetal? Explain your answer.

Electronegativity and the Reactivities of the Elements

9.38 When we say that aluminum is more *reactive* than iron, which kind of reaction of these elements are we describing?

9.39 In what groups in the periodic table are the most reactive metals found? Where do we find the least reactive metals?

9.40 How is the electronegativity of a metal related to its reactivity?

9.41 Arrange the following metals in their approximate order of reactivity (most reactive first, least reactive last) based on their locations in the periodic table: **(a)** iridium, **(b)** silver, **(c)** calcium, **(d)** iron.

9.42 Complete and balance the following equations. If no reaction occurs, write "N.R."

(a) $KCl + Br_2 \longrightarrow$
(b) $NaI + Cl_2 \longrightarrow$
(c) $KCl + F_2 \longrightarrow$
(d) $CaBr_2 + Cl_2 \longrightarrow$
(e) $AlBr_3 + F_2 \longrightarrow$
(f) $ZnBr_2 + I_2 \longrightarrow$

9.43 In each pair, choose the better oxidizing agent.

(a) O_2 or F_2
(b) As_4 or P_4
(c) Br_2 or I_2
(d) P_4 or S_8
(e) Se_8 or Cl_2
(f) As_4 or S_8

Failure of the Octet Rule

9.44 How many electrons are in the valence shells of **(a)** Be in $BeCl_2$, **(b)** B in BCl_3, and **(c)** H in H_2O?

9.45 What is the minimum number of electrons that would be expected to be in the valence shell of As, in $AsCl_5$?

9.46 Nitrogen and arsenic are in the same group in the periodic table. Arsenic forms both $AsCl_3$ and $AsCl_5$, but with chlorine, nitrogen only forms NCl_3. On the basis of the electronic structures of N and As, explain why this is so.

Bond Length and Bond Energy

9.47 Define *bond length* and *bond energy*.

9.48 Define *bond order*. How are bond energy and bond length related to bond order? Why are there these relationships?

9.49 The energy required to break the H—Cl bond to give H^+ and Cl^- ions would not be called the H—Cl bond energy. Why?

Formal Charge

9.50 What is the definition of *formal charge*?

9.51 How are formal charges used to select the best Lewis structure for a molecule? What is the basis for this method of selection?

9.52 What are the formal charges on the atoms in the HCl molecule? What are the actual charges on the atoms in this molecule? (*Hint:* See Section 9.6.) Are formal charges the same as actual charges?

Coordinate Covalent Bonds

9.53 What is a *coordinate covalent bond*?

9.54 Once formed, how (if at all) does a coordinate covalent bond differ from an ordinary covalent bond?

9.55 BCl_3 has an incomplete valence shell. Use Lewis structures to show how it could form a coordinate covalent bond with a water molecule.

Resonance

9.56 Why is the concept of resonance needed?

9.57 What is a resonance hybrid? How does it differ from the resonance structures drawn for a molecule?

9.58 Draw the resonance structures of the benzene molecule. Why is benzene more stable than one would expect if the ring contained three carbon–carbon double bonds?

9.59 Polystyrene plastic is a hydrocarbon that consists of a long chain of carbon atoms joined by single bonds in which every other carbon is attached to a benzene ring. The ring is attached by replacing a hydrogen of benzene with a single bond to the carbon chain. Sketch a portion of a polystyrene molecule that contains five benzene rings.

Review Problems

Lattice Energy

9.60 Use data from the tables of ionization energies and electron affinities on pages 343 and 348 to calculate the energy changes for the following reactions.

$$Na(g) + Cl(g) \longrightarrow Na^+(g) + Cl^-(g)$$
$$Na(g) + 2Cl(g) \longrightarrow Na^{2+}(g) + 2Cl^-(g)$$

Approximately how many times larger would the lattice energy of $NaCl_2$ have to be compared to the lattice energy of NaCl for $NaCl_2$ to be more stable than NaCl?

9.61 Changing 1 mol of Mg(*s*) and 1/2 mol of $O_2(g)$ to gaseous atoms requires a total of approximately 150 kJ of energy. The first and second ionization energies of magnesium are 737 and 1450 kJ/mol, respectively; the first and second electron affinities of oxygen are −141 and +844 kJ/mol, respectively; and the standard heat of formation of MgO(*s*) is −602 kJ/mol. Construct an enthalpy diagram similar to the one in Figure 9.4 (page 360) and use it to calculate the lattice energy of magnesium oxide. How does the lattice energy of MgO compare with that of NaCl? What might account for the difference?

Electron Configurations of Ions

9.62 Explain what happens to the electron configurations of Mg and Br when they react to form magnesium bromide.

9.63 Describe what happens to the electron configurations of lithium and nitrogen when they react to form the lithium nitride.

ILW OH **9.64** What are the electron configurations of the Pb^{2+} and Pb^{4+} ions?

9.65 What are the electron configurations of the Bi^{3+} and Bi^{5+} ions?

9.66 Write the abbreviated electron configuration of the Mn^{3+} ion. How many unpaired electrons does the ion contain?

9.67 Write the abbreviated electron configuration of the Co^{3+} ion. How many unpaired electrons does the ion contain?

Lewis Symbols

9.68 Write Lewis symbols for the following atoms: **(a)** Si, **(b)** Sb, **(c)** Ba, **(d)** Al, **(e)** S.

9.69 Write Lewis symbols for the following atoms: **(a)** K, **(b)** Ge, **(c)** As, **(d)** Br, **(e)** Se.

9.70 Use Lewis symbols to diagram the reactions between **(a)** Ca and Br, **(b)** Al and O, and **(c)** K and S.

OH **9.71** Use Lewis symbols to diagram the reactions between **(a)** Mg and S, **(b)** Mg and Cl, and **(c)** Mg and N.

Dipole Moments

9.72 Use the data in Table 9.3 (page 378) to calculate the amount of charge on the oxygen and nitrogen in the nitrogen monoxide molecule, expressed in electronic charge units ($e = 1.60 \times 10^{-19}$ C). Which atom carries the positive charge?

9.73 The molecule bromine monofluoride has a dipole moment of 1.42 D and a bond length of 176 pm. Calculate the charge on the ends of the molecule, expressed in electronic charge units ($e = 1.60 \times 10^{-19}$ C). Which atom carries the positive charge?

9.74 The dipole moment of HF is 1.83 D and the bond length is 917 pm. Calculate the amount of charge (in electronic charge units) on the hydrogen and the fluorine atoms in the HF molecule.

OH **9.75** In the vapor state, cesium and fluoride ions pair to give CsF formula units that have a bond length of 0.255 nm and a dipole moment of 7.88 D. What is the actual charge on the cesium and fluorine atoms in CsF? What percentage of full 1+ and 1− charges is this?

Bond Energy

9.76 How much energy, in joules, is required to break the bond in *one* chlorine molecule? The bond energy of Cl_2 is 242.6 kJ/mol.

9.77 How much energy is released in the formation of one molecule of HCl by the following reaction?

$$H^+(g) + Cl^-(g) \longrightarrow HCl(g)$$

The bond energy of HCl is 431 kJ mol^{-1}. Additional data can be found in tables in Chapter 8.

9.78 The reason there is danger in exposure to high-energy radiation (e.g., ultraviolet and X rays) is that the radiation can rupture chemical bonds. In some cases, cancer can be caused by it. A carbon–carbon single bond has a bond energy of approximately 348 kJ per mole. What wavelength of light is required to provide sufficient energy to break the C—C bond? In which region of the electromagnetic spectrum is this wavelength located?

9.79 A mixture of H_2 and Cl_2 is stable, but a bright flash of light passing through it can cause the mixture to explode. The light causes Cl_2 molecules to split into Cl atoms, which are highly reactive. What wavelength of light is necessary to cause the Cl_2 molecules to split? The bond energy of Cl_2 is 242.6 kJ per mole.

Covalent Bonds and the Octet Rule

9.80 Use Lewis structures to diagram the formation of **(a)** Br_2, **(b)** H_2O, and **(c)** NH_3 from neutral atoms.

OH **9.81** Chlorine tends to form only one covalent bond because it needs just one electron to complete its octet. What are the Lewis structures for the simplest compound formed by chlorine with **(a)** nitrogen, **(b)** carbon, **(c)** sulfur, and **(d)** bromine?

9.82 Use the octet rule to predict the formula of the simplest compound formed from hydrogen and **(a)** selenium, **(b)** arsenic, and **(c)** silicon. (Remember that the valence shell of hydrogen can hold only two electrons.)

9.83 What would be the formula for the simplest compound formed from **(a)** phosphorus and chlorine, **(b)** carbon and fluorine, and **(c)** iodine and chlorine?

Electronegativity

9.84 Use Figure 9.9 to choose the atom in each of the following bonds that carries the partial positive charge: **(a)** N—S, **(b)** Si—I, **(c)** N—Br, **(d)** C—Cl.

9.85 Use Figure 9.9 to choose the atom that carries the partial negative charge in each of the following bonds: **(a)** Hg—I, **(b)** P—I, **(c)** Si—F, **(d)** Mg—N.

9.86 Which of the bonds in Problem 9.84 is the most polar?

9.87 Which of the bonds in the Problem 9.85 is the least polar?

Drawing Lewis Structures

ILW **9.88** Draw Lewis structures for **(a)** $AsCl_4^+$, **(b)** ClO_2^-, **(c)** HNO_2, and **(d)** XeF_2.

9.89 Draw Lewis structures for **(a)** TeF_4, **(b)** ClF_5, **(c)** PF_6^-, and **(d)** XeF_4.

9.90 Draw Lewis structures for **(a)** $SiCl_4$, **(b)** PF_3, **(c)** PH_3, and **(d)** SCl_2.

9.91 Draw Lewis structures for **(a)** HIO_3, **(b)** H_2CO_3, **(c)** HCO_3^-, and **(d)** PCl_4^+.

9.92 Draw Lewis structures for **(a)** carbon disulfide and **(b)** cyanide ion.

9.93 Draw Lewis structures for **(a)** selenium trioxide and **(b)** selenium dioxide.

9.94 Draw Lewis structures for **(a)** AsH_3, **(b)** $HClO_2$, **(c)** H_2SeO_3, and **(d)** H_3AsO_4.

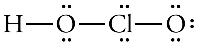
OH **9.95** Draw Lewis structures for **(a)** NO^+, **(b)** NO_2^-, **(c)** $SbCl_6^-$, and **(d)** IO_3^-.

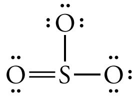
9.96 Draw the Lewis structure for **(a)** CH_2O (the central atom is carbon, which is attached to two hydrogens and an oxygen), and **(b)** $SOCl_2$ (the central atom is sulfur, which is attached to an oxygen and two chlorines).

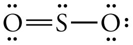
9.97 Draw Lewis structures for **(a)** $GeCl_4$, **(b)** CO_3^{2-}, **(c)** PO_4^{3-}, and **(d)** O_2^{2-}.

Formal Charge

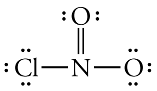
9.98 Assign formal charges to each atom in the following structures:

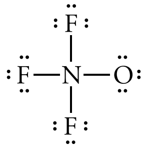
(a)


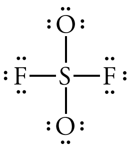
(b)


(c)


9.99 Assign formal charges to each atom in the following structures:

(a)


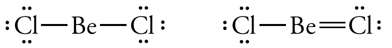
(b)


(c)


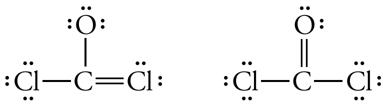
ILW **9.100** Draw the Lewis structure for $HClO_4$ according to the procedure described in Figure 9.12. Assign formal charges to each atom in the formula. Determine the preferred Lewis structure for this compound.

9.101 Draw the Lewis structure for SO_2Cl (sulfur bonded to two Cl and one O). Assign formal charges to each atom. Determine the preferred Lewis structure for this molecule.

9.102 Below are two structures for $BeCl_2$. Give two reasons why the one on the left is the preferred structure.



9.103 The following are two Lewis structures that can be drawn for phosgene, a substance that has been used as a war gas.



Which is the better Lewis structure? Why?

Coordinate Covalent Bonds

9.104 Use Lewis structures to show that the hydronium ion, H_3O^+, can be considered to be formed by the creation of a coordinate covalent bond between H_2O and H^+.

9.105 Use Lewis structures to show that the reaction

$$BF_3 + F^- \longrightarrow BF_4^-$$

involves the formation of a coordinate covalent bond.

Resonance

9.106 Draw the resonance structures for CO_3^{2-}. Calculate the average C—O bond order.

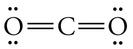
ILW **9.107** Draw all of the resonance structures for the N_2O_4 molecule and determine the average N—O bond order. The skeletal structure of the molecule is

O O
N N
O O

OH **9.108** How should the N—O bond lengths compare in the NO_3^- and NO_2^- ions?

9.109 Arrange the following in order of increasing C—O bond length: CO, CO_3^{2-}, CO_2, HCO_2^- (formate ion, page 394).

9.110 The Lewis structure of CO_2 was given as



but two other resonance structures can also be drawn for it. What are they? On the basis of formal charges, why are they not preferred structures?

9.111 Use formal charges to establish the preferred Lewis structures for the ClO_3^- and ClO_4^- ions. Draw resonance structures for both ions and determine the average Cl—O bond order in each. Which of these ions would be expected to have the shorter Cl—O bond length?

Additional Exercises

9.112 Use an enthalpy diagram to calculate the lattice energy of $CaCl_2$ from the following information. Energy needed to vaporize one mole of Ca(*s*) is 192 kJ. For calcium, the first IE = 589.5 kJ mol^{-1}, the second IE = 1146 kJ mol^{-1}. The electron affinity of Cl is 348 kJ mol^{-1}. The bond energy of Cl_2 is 242.6 kJ per mole of Cl—Cl bonds. The standard heat of formation of $CaCl_2$ is −795 kJ mol^{-1}.

9.113 Use an enthalpy diagram and the following data to calculate the electron affinity of bromine. The standard heat of formation of NaBr is −360 kJ mol^{-1}. The energy needed to vaporize one mole of $Br_2(l)$ to give $Br_2(g)$ is 31 kJ mol^{-1}. The first ionization energy of Na is 495.4 kJ mol^{-1}. The bond energy of Br_2 is 192 kJ per mole of Br–Br bonds. The lattice energy of NaBr is −743.3 kJ mol^{-1}.

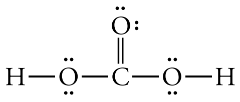
9.114 In many ways, tin(IV) chloride behaves more like a covalent molecular species than like a typical ionic chloride. Draw the Lewis structure for the tin(IV) chloride molecule.

9.115 In each pair, choose the one with the more polar bonds. (Use the periodic table to answer the question.)

(a) PCl_3 or $AsCl_3$
(b) SF_2 or GeF_4
(c) $SiCl_4$ or SCl_2
(d) SrO or SnO

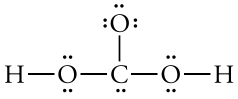
9.116 How many electrons are in the outer shell of the Zn^{2+} ion?

9.117 The Lewis structure for carbonic acid (formed when CO_2 dissolves in water) is usually given as

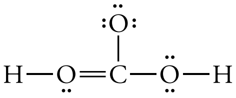


$$\begin{array}{c} \ddot{O}: \\ \| \\ H-\ddot{O}-C-\ddot{O}-H \end{array}$$

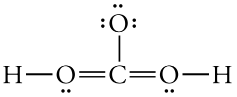
What is wrong with the following structures?

(a)


$$\begin{array}{c} :\ddot{O}: \\ | \\ H-\ddot{O}-\underset{..}{C}-\ddot{O}-H \end{array}$$

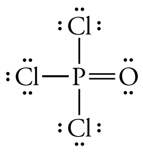
(b)


$$\begin{array}{c} :\ddot{O}: \\ | \\ H-\underset{..}{O}=C-\ddot{O}-H \end{array}$$

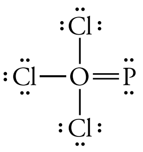
(c)


$$\begin{array}{c} :\ddot{O}: \\ | \\ H-\underset{..}{O}=C=\underset{..}{O}-H \end{array}$$

9.118 Are the following Lewis structures considered to be resonance structures? Explain. Which is the more likely structure for $POCl_3$?



$$\begin{array}{c} :\ddot{Cl}: \\ | \\ :\ddot{Cl}-P=\ddot{O} \\ | \\ :\ddot{Cl}: \end{array}$$



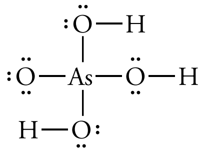
$$\begin{array}{c} :\ddot{Cl}: \\ | \\ :\ddot{Cl}-O=\ddot{P} \\ | \\ :\ddot{Cl}: \end{array}$$

9.119 Assign formal charges to all the atoms in the following Lewis structure of hydrazoic acid, HN_3.

$$H-N\equiv N-\underset{..}{\ddot{N}}:$$

Suggest a lower-energy resonance structure for this molecule.

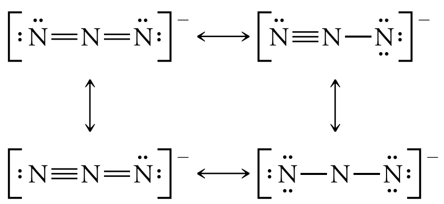
9.120 Assign formal charges to all the atoms in the Lewis structure



$$\begin{array}{c} :\ddot{O}-H \\ | \\ :\ddot{O}-As-\ddot{O}-H \\ | \\ H-\ddot{O}: \end{array}$$

Suggest a lower-energy Lewis structure for this molecule.

9.121 The inflation of an "air bag" when a car experiences a collision occurs by the explosive decomposition of sodium azide, NaN_3, which yields nitrogen gas that inflates the bag. The following resonance structures can be drawn for the azide ion, N_3^-. Identify the best and worst of them.



9.122 How should the sulfur–oxygen bond lengths compare for the species SO_3, SO_2, SO_3^{2-}, and SO_4^{2-}?

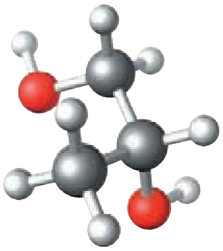
9.123 What is the most reasonable Lewis structure for S_2Cl_2?

***9.124** There are two acids that have the formula HCNO. Which of the following skeletal structures are most likely for them? Justify your answer.

HCON HNOC HOCN
HCNO HNCO HONC

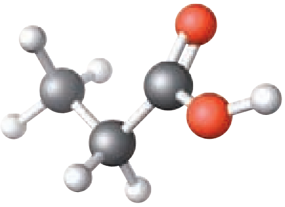
9.125 In the vapor state, ion pairs of KF can be identified. The dipole moment of such a pair is measured to be 8.59 D and the K—F bond length is found to be 217 pm. Is the K—F bond 100% ionic? If not, what percent of full 1+ and 1− charges do the K and F atoms carry, respectively?

9.126 Below is a ball-and-stick model of a type of alcohol derived from a hydrocarbon. What is the formula for the hydrocarbon and what is its name?

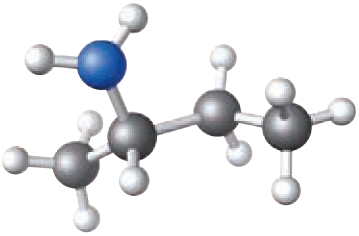


Multi-Concept Problems

9.127 Use Lewis structures to show the ionization of the following organic acid (a weak acid) in water.



9.128 The compound below is called an amine. It is a weak base and undergoes ionization in water following a path similar to that of ammonia. Use Lewis structures to diagram the reaction of this amine with water.



9.129 Use Lewis structures to diagram the reaction between the acid in Problem 9.127 with the base in Problem 9.128. If 12.5 g of the acid is mixed with 17.4 g of the base, how many grams of which reactant will remain unreacted after the reaction is complete?

9.130 How many grams of water could have its temperature raised from 25 °C (room temperature) to 100 °C (the boiling point of water) by the amount of energy released in the formation of 1 mol of H_2 from hydrogen atoms? The bond energy of H_2 is 435 kJ/mol.

***9.131** What wavelength of light, if absorbed by a hydrogen molecule, could cause the molecule to split into the ions H^+ and H^-? (The data required are available in this and previous chapters.)

***9.132** A 38.40 mg sample of an organic acid composed of just carbon, hydrogen, and oxygen was burned in pure oxygen to give 37.54 mg CO_2 and 7.684 mg H_2O in a combustion analysis. In a separate experiment, the molecular mass was determined to be 90. In a titration, 40.2 mg of the acid dissolved in 50 mL of water required 14.28 mL of 0.0625 *M* NaOH for complete neutralization. Use these data to draw a reasonable Lewis structure for the compound.

Exercises in Critical Thinking

9.133 What is the average bond energy of a C—C covalent bond? What wavelength of light provides enough energy to break such a bond? Using this information, explain why unfiltered sunlight is damaging to the skin.

9.134 One way of estimating the electronegativity of an atom is to use an average of its ionization energy and electron affinity. Why would these two quantities, taken together, be related to electronegativity?

9.135 The attractions between molecules of a substance can be associated with the size of the molecule's dipole moment. Explain why this is so.

9.136 The positive end of the dipole in a water molecule is not located on an atom. Explain why this happens and suggest other simple molecules that show the same effect.

9.137 In describing the structures of molecules, we use Lewis structures, formal charges, and experimental evidence. Rank these in terms of importance in deciding on the true structure of a molecule, and defend your choice.

10 Theories of Bonding and Structure

In preceding chapters you've seen a variety of molecular shapes illustrated by molecular drawings. Molecular shape has many important consequences, among them our ability to detect odors, both pleasant and unpleasant. Olfactory receptors in our nasal passages bind selectively to molecules according to their shapes. The receptors then send signals to the brain that permit us to distinguish among an enormous number of odor molecules, including those that skunks use to defend themselves. In this chapter we will examine the nature of the shapes of molecules as well as theories of bonding that permit us to explain and sometimes predict molecular geometry. © Corbis RF/Alamy

Chapter Outline

10.1 | Five Basic Molecular Geometries

10.2 | Molecular Shapes and the VSEPR Model

10.3 | Molecular Structure and Dipole Moments

10.4 | Valence Bond Theory

10.5 | Hybrid Orbitals and Molecular Geometry

10.6 | Hybrid Orbitals and Multiple Bonds

10.7 | Molecular Orbital Theory Basics

10.8 | Delocalized Molecular Orbitals

10.9 | Bonding in Solids

10.10 | Atomic Size and the Tendency toward Multiple Bond Formation

This Chapter in Context

The structure of a solid ionic compound, such as NaCl, is controlled primarily by the sizes of the ions and their charges. The attractions between the ions have no preferred directions, so if an ionic compound is melted, this structure is lost and the ordered array of ions collapses into a jumbled liquid state. Molecular substances are quite different, however. Molecules have three-dimensional shapes that are determined by the relative orientations of their covalent bonds, and this structure is maintained regardless of whether the substance is a solid, a liquid, or a gas. You've seen some of these shapes in previous chapters.

Many of the properties of a molecule depend on the three-dimensional arrangement of its atoms. As described in the caption accompanying the chapter-opening photo, we detect various aromas because of a precise fit between "odor molecules" and odor receptors in our olfactory system. Similarly, the structures of polymer molecules in plastics have a strong influence on the properties of materials made from them.

In this chapter we will explore the topic of molecular geometry and study theoretical models that allow us to explain, and in some cases predict, the shapes of molecules. We will also examine theories that explain, in terms of wave mechanics and the electronic structures of atoms, *how* covalent bonds form and *why* they are so highly directional in nature. You will find the knowledge gained here helpful in later discussions of the physical properties of substances such as melting points and boiling points.

10.1 | Five Basic Molecular Geometries

Although we live in a three-dimensional world made up of three-dimensional molecules, the Lewis structures we've been using to describe the bonding in molecules do not convey any information about shape. They simply describe which atoms are bonded to each other. Our goal now is to examine theories that predict molecular shapes and explain covalent structures in terms of quantum theory. We begin by describing some of the kinds of shapes molecules have.

Molecular shape only becomes a question when there are at least three atoms present. If there are only two, there is no doubt as to how they are arranged; one is just alongside the other. But when there are three or more atoms in a molecule we find that its shape is often built from just one or another of five basic geometrical structures.

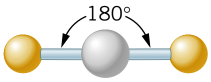
■ As you study these structures, you should try hard to visualize them in three dimensions. You should also learn how to sketch them in a way that conveys the three-dimensional information.

TOOLS

Basic molecular shapes

Linear Molecules

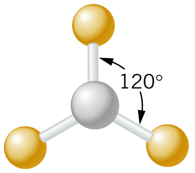
In a **linear molecule** the atoms lie in a straight line. When the molecule has three atoms, the angle formed by the covalent bonds, which we call the **bond angle**, equals 180° as illustrated below.



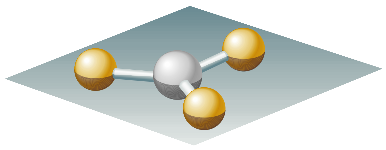
A linear molecule

Planar Triangular Molecules

A **planar triangular molecule** is one in which three atoms are located at the corners of a triangle and are bonded to a fourth atom that lies in the center of the triangle.



A planar triangular molecule

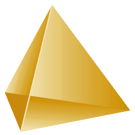


Another view showing how all the atoms are in the same plane

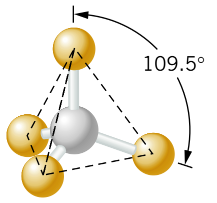
In this molecule, all four atoms lie in the same plane and the bond angles are all equal to 120°.

Tetrahedral Molecules

A **tetrahedron** is a four-sided geometric figure shaped like a pyramid with triangular faces. A **tetrahedral molecule** is one in which four atoms, located at the vertices of a tetrahedron, are bonded to a fifth atom in the center of the structure.



A tetrahedron

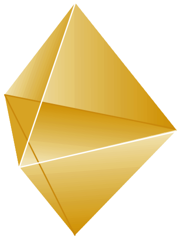


A tetrahedral molecule

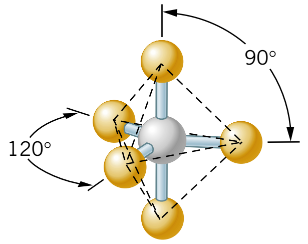
All of the bond angles in a tetrahedral molecule are the same and are equal to 109.5°.

Trigonal Bipyramidal Molecules

A **trigonal bipyramid** consists of two *trigonal pyramids* (pyramids with triangular faces) that share a common base. In a **trigonal bipyramidal molecule**, the central atom is located in the middle of the triangular plane shared by the upper and lower trigonal pyramids and is bonded to five atoms that are at the vertices of the figure.



A trigonal bipyramid



A trigonal bipyramidal molecule

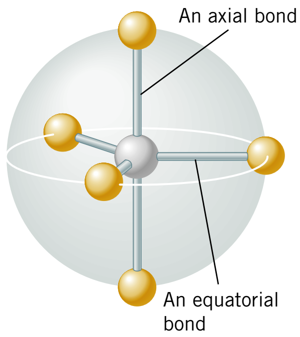


Figure 10.1 | **Axial and equatorial bonds in a trigonal bipyramidal molecule.**

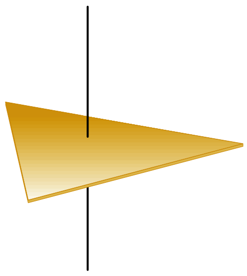


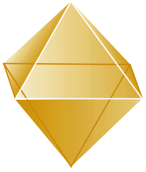
Figure 10.2 | **A simplified way of drawing a trigonal bipyramid.** To form a trigonal bipyramidal molecule, atoms would be attached at the corners of the triangle in the center and at the ends of the bonds that extend vertically up and down.

In this molecule, not all the bonds are equivalent. If we imagine the trigonal bipyramid centered inside a sphere similar to earth, as illustrated in Figure 10.1, the atoms in the triangular plane are located around the equator. The bonds to these atoms are called **equatorial bonds**. The angle between any two equatorial bonds is 120°. The two vertical bonds pointing along the north and south axis of the sphere are 180° apart and are called **axial bonds**. The bond angle between an axial bond and an equatorial bond is 90°.

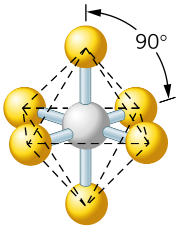
A simplified representation of a trigonal bipyramid is illustrated in Figure 10.2. The equatorial triangular plane is sketched as it would look tilted backward, so we're looking at it from its edge. The axial bonds are represented as lines pointing up and down. To add more three-dimensional character, notice that the bond pointing down appears to be partially hidden by the triangular plane in the center.

Octahedral Molecules

An **octahedron** is an eight-sided figure, which you might think of as two *square pyramids* sharing a common square base. The octahedron has only six vertices, and in an **octahedral molecule** we find an atom in the center of the octahedron bonded to six other atoms at the vertices.



An octahedron



An octahedral molecule

All of the bonds in an octahedral molecule are equivalent, with angles between adjacent bonds equal to 90°.

A simplified representation of an octahedron is shown in Figure 10.3. The square plane in the center of the octahedron, when drawn in perspective and viewed from its edge, looks like a parallelogram. The bonds to the top and bottom of the octahedron are shown as vertical lines. Once again, the bond pointing down is drawn so it appears to be partially hidden by the square plane in the center.

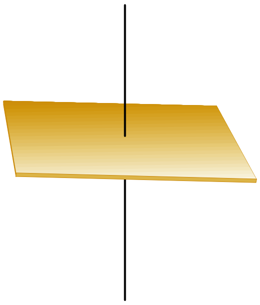


Figure 10.3 | **A simplified way of drawing an octahedron.** To form an octahedral molecule, atoms would be attached at the corners of the square in the center and at the ends of the bonds that extend vertically up and down.

10.2 | Molecular Shapes and the VSEPR Model

In general, a useful theoretical model should explain known facts, and it should be capable of making accurate predictions. The **valence shell electron pair repulsion model** (called the **VSEPR model,** for short) is remarkably successful at both and is also conceptually simple. The model is based on the following idea:

> Electron pairs (or groups of electron pairs) in the valence shell of an atom repel each other and will position themselves so that they are as far apart as possible, thereby minimizing the repulsions.

TOOLS

VSEPR model

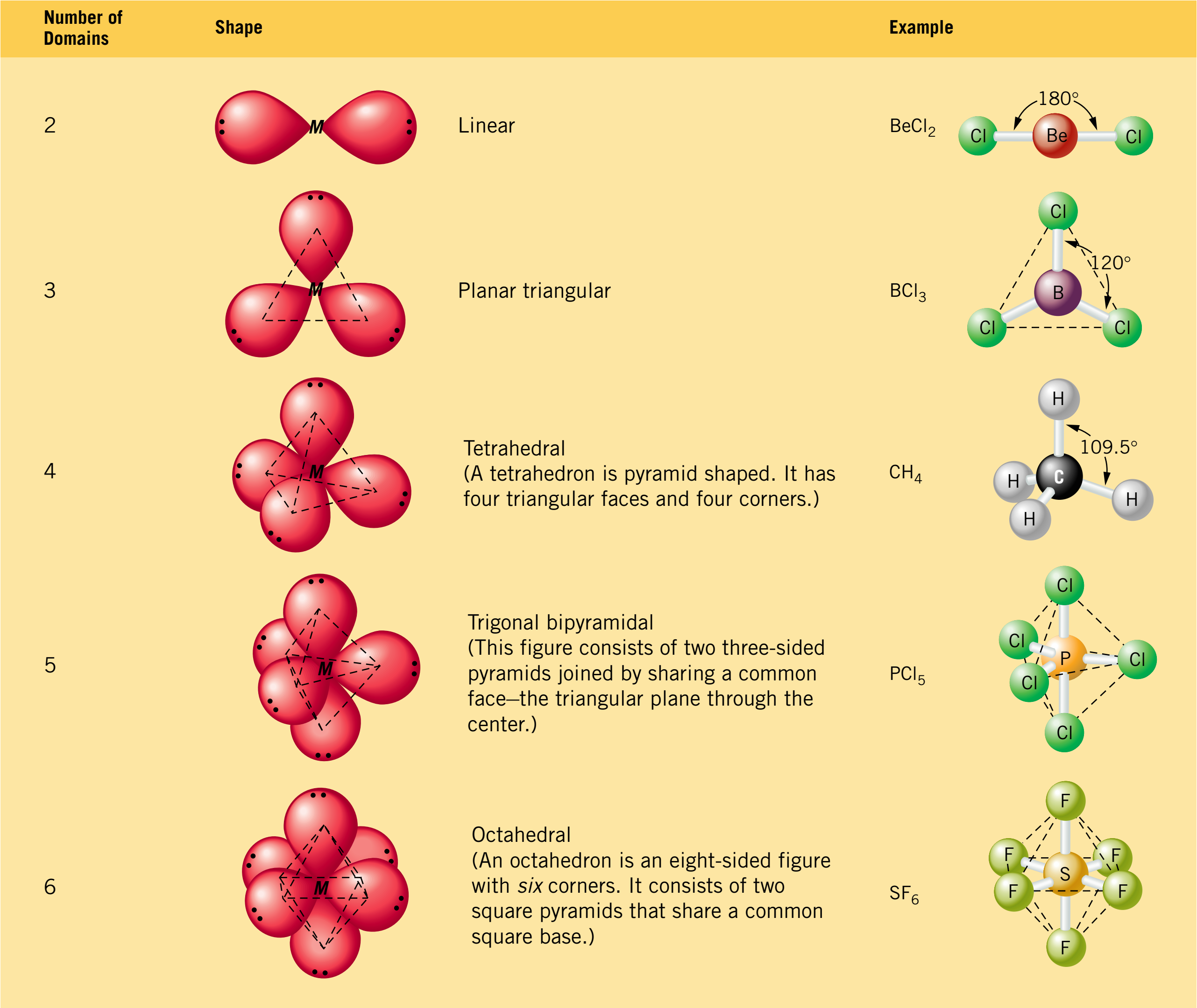
The term we will use to describe the space occupied by a group of electrons in the valence shell of an atom is **electron domain,** so the preceding statement can be rephrased as: *electron domains stay as far apart as possible so as to minimize their mutual repulsions.*

As you will see, in describing the shapes of molecules it is useful to divide electron domains into two categories—domains that contain electrons in bonds and domains that contain unshared electrons. They are called *bonding domains* and *nonbonding domains*, respectively.

- A **bonding domain** contains the electrons that are shared between two atoms. *Therefore, all of the electrons within a given single, double, or triple bond are considered to be in the same bonding domain.* A double bond (containing 4 electrons) will occupy more space than a single bond (with only 2 electrons) but all electrons shared by the atoms occupy the same general region in space, so they all belong to the same bonding domain.
- A **nonbonding domain** contains valence electrons that are associated with *a single atom.* A nonbonding domain is either an unshared pair of valence electrons (called a **lone pair**) or, in some cases, a single unpaired electron (found in molecules with an odd number of valence electrons).

■ An ***electron domain*** can be a bond, a lone pair, or an unpaired electron. Some prefer to call the VSEPR model (or VSEPR theory) the *electron domain model.*

Figure 10.4 shows the orientations assumed by different numbers of electron domains, which permit them to minimize repulsions by remaining as far apart as possible. These



Number of Domains	Shape		Example
2		Linear	$BeCl_2$
3		Planar triangular	BCl_3
4		Tetrahedral (A tetrahedron is pyramid shaped. It has four triangular faces and four corners.)	CH_4
5		Trigonal bipyramidal (This figure consists of two three-sided pyramids joined by sharing a common face—the triangular plane through the center.)	PCl_5
6		Octahedral (An octahedron is an eight-sided figure with *six* corners. It consists of two square pyramids that share a common square base.)	SF_6

Figure 10.4 | **Shapes expected for different numbers of electron domains around a central atom, *M*.** Each lobe represents an electron domain.

same orientations are achieved whether the domains are bonding or nonbonding. If all of them are bonding domains, molecules are formed having the shapes described in the preceding section, as shown at the right in Figure 10.4.

Lewis Structures and the VSEPR Model

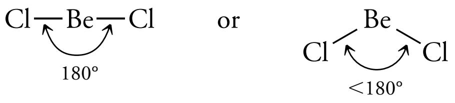
To apply the VSEPR model in predicting shape, we have to know how many electron domains are in the valence shell of the central atom. This is where Lewis structures are especially helpful.

■ In Chapter 9 we noted that the bonds in $BeCl_2$ are covalent, rather than ionic.

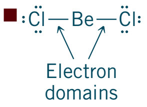
Consider the $BeCl_2$ molecule. On page 383 we gave its Lewis structure as

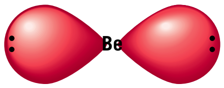
$$:\underset{..}{\overset{..}{Cl}}-Be-\underset{..}{\overset{..}{Cl}}:$$

Because there are just three atoms, only two shapes are possible. The molecule must be either linear or nonlinear; that is, the atoms lie in a straight line, or they form some angle less than 180°.



To predict the structure, we begin by counting the number of electron domains in the valence shell of the Be atom. In this molecule Be forms two single bonds to Cl atoms, so Be has two bonding domains in its valence shell. In Figure 10.4, we see that when there are two electron domains in the valence shell of an atom, minimum repulsion occurs if they are on opposite sides of the nucleus, pointing in opposite directions. We can represent this as





to suggest the approximate locations of the electron clouds of the valence shell electron pairs. In order for the electrons to be in the Be—Cl bonds, the Cl atoms must be placed where the electrons are; the result is that we predict that a $BeCl_2$ molecule should be linear.

$$Cl—Be—Cl$$

Experimentally it has been shown that this is the shape of $BeCl_2$ molecules in the vapor state.

Example 10.1

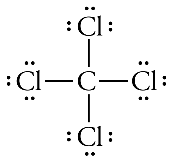
Predicting Molecular Shapes

Carbon tetrachloride was once used as a cleaning fluid until it was discovered that it causes liver damage if absorbed by the body. What is the shape of the molecule?

Analysis: To find the shape of the molecule, we need its Lewis structure so that we can count electron domains and apply the VSEPR model. To write the Lewis structure, we need the formula for the compound, and that requires the application of the rules of chemical nomenclature.

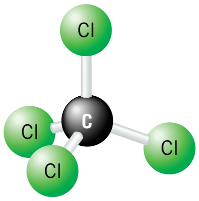
Assembling the Tools: The primary tool for solving this kind of problem is the Lewis structure, which we will draw following the procedure in Chapter 9. First, however, we need the chemical formula. Applying the rules of nomenclature in Chapter 3 gives CCl_4. Finally, we'll use the VSEPR model as a tool to deduce the structure of the molecule.

Solution: Following the procedure in Figure 9.12, the Lewis structure of CCl_4 is



$$\begin{array}{ccccc} & & :\ddot{\underset{..}{Cl}}: & & \\ & & | & & \\ :\ddot{\underset{..}{Cl}} & — & C & — & \ddot{\underset{..}{Cl}}: \\ & & | & & \\ & & :\ddot{\underset{..}{Cl}}: & & \end{array}$$

There are four bonds, each corresponding to a bonding domain around the carbon. According to Figure 10.4, the domains can be farthest apart when arranged tetrahedrally, so the molecule is expected to be tetrahedral. (This is, in fact, its structure.)



Is the Answer Reasonable? The answer depends critically on the Lewis structure, so be sure to check that you've constructed it correctly. Once we're confident in the Lewis structure the rest is straightforward. The arrangement of domains gives us the arrangement of Cl atoms around the C atom.

Practice Exercises

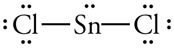
10.1 | What is the shape of the SeF_6 molecule? (*Hint:* If necessary, refer to Figure 9.12 on page 384.)

10.2 | What shape is expected for the $SbCl_5$ molecule?

Nonbonding Domains and Molecular Shapes

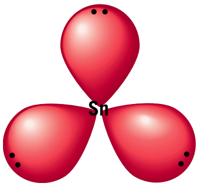
Some molecules have a central atom with one or more nonbonding domains, each of which consists of an unshared electron pair (lone pair) or a single unpaired valence electron. These nonbonding domains affect the geometry of the molecule. An example is $SnCl_2$.

■ The electronegativity difference between tin and chlorine is only 1.1, which means that tin–chlorine bonds have a significant degree of covalent character. Many compounds of tin are molecular, especially those of Sn^{IV}. $SnCl_2$ is another example of a molecule that behaves as though it has less than an octet around the central atom.

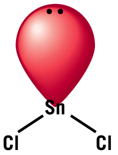


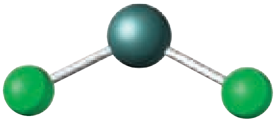
$$:\underset{\cdot\cdot}{\ddot{Cl}}-\ddot{Sn}-\underset{\cdot\cdot}{\ddot{Cl}}:$$

There are *three* domains around the tin atom: two bonding domains plus a nonbonding domain (the lone pair). According to Figure 10.4, the domains are farthest apart when at the corners of a triangle. For the moment, let's ignore the chlorine atoms and concentrate on how the electron domains are arranged.



We can find the shape of the molecule, now, by placing the two Cl atoms where two of the domains are (below, left).



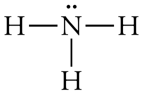


We can't describe this molecule as triangular, even though that is how the domains are arranged. ***Molecular shape describes the arrangement of atoms, not the arrangement of electron domains.*** Therefore, to describe the shape we ignore the lone pair, as shown above at the right, and say that the $SnCl_2$ molecule has a structure that is **nonlinear** or **bent** or **V-shaped**.

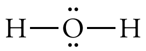
Notice that when there are three domains around the central atom, *two* different molecular shapes are possible. If all three are bonding domains, a molecule with a planar triangular shape is formed, as shown for BCl_3 in Figure 10.4. If one of the domains is nonbonding, as in $SnCl_2$, the arrangement of the atoms in the molecule is said to be nonlinear. The predicted shapes of both, however, are *derived* by first noting the triangular arrangement of domains around the central atom and *then* adding the necessary number of atoms.

Molecules with Four Electron Domains around the Central Atom

There are many molecules with four electron pairs (an octet) in the valence shell of the central atom. When these electron pairs are used to form four single bonds, as in methane (CH_4), the resulting molecule is tetrahedral (Figure 10.4). There are many examples, however, where nonbonding domains are also present. For instance, two molecules you've encountered before are



one lone pair



$$H-\underset{\cdot\cdot}{\ddot{O}}-H$$

two lone pairs

Figure 10.5 shows how the nonbonding domains affect the shapes of molecules of this type.

With one nonbonding domain, as in NH_3, the central atom is at the top of a pyramid with three atoms at the corners of the triangular base. The resulting structure is said to be **trigonal pyramidal**. When there are two nonbonding domains in the tetrahedron, as in H_2O,

■ Note once again that in describing the shape of the molecule, we look at how the atoms are arranged and ignore the nonbonding domains.

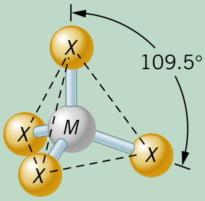
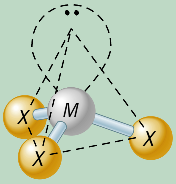
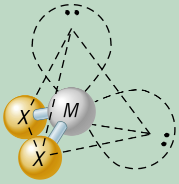
Number of Bonding Domains	Number of Nonbonding Domains	Structure	
4	0		**Tetrahedral** (example, CH_4) All bond angles are 109.5°.
3	1		**Trigonal pyramidal** (pyramid shaped) (example, NH_3)
2	2		**Nonlinear, bent** (example, H_2O)

Figure 10.5 | **Molecular shapes with four domains around the central atom.** The molecules MX_4, MX_3, and MX_2 shown here all have four domains arranged tetrahedrally around the central atom. The names used to describe the shapes are derived from the way the X atoms are arranged around M, ignoring the nonbonding domains.

the three atoms of the molecule (the central atom plus the two atoms bonded to it) do not lie in a straight line, so the structure is described as nonlinear or bent.

Molecules with Five Electron Domains around the Central Atom

When five domains are present around the central atom, they are directed toward the vertices of a trigonal bipyramid. Molecules such as PCl_5 have this geometry, as shown in Figure 10.4, and are said to have a **trigonal bipyramidal** shape.

In the trigonal bipyramid, nonbonding domains always occupy positions in the *equatorial plane* (the triangular plane through the center of the molecule). This is because nonbonding domains, which have a positive nucleus only at one end, are larger than bonding domains, as illustrated in Figure 10.6. The larger nonbonding domains are less crowded in the equatorial plane, where they have just two closest neighbors at 90°, than they would be in an axial position, where they would have three closest neighbors at 90°.

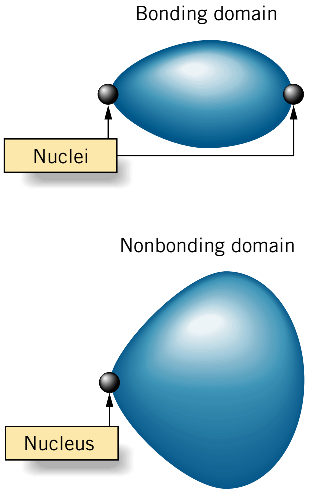


Figure 10.6 | **Relative sizes of bonding and nonbonding domains.**

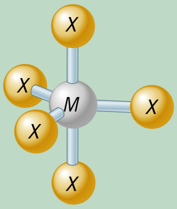
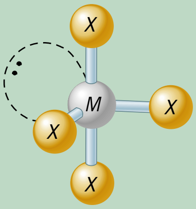
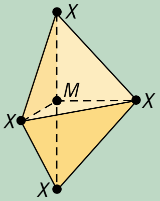
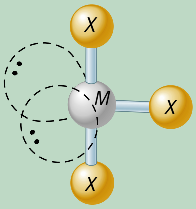
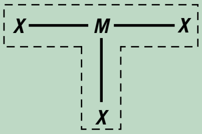
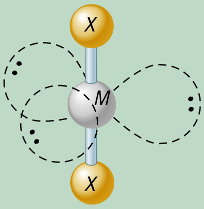
Number of Bonding Domains	Number of Nonbonding Domains	Structure
5	0	 **Trigonal bipyramidal** (example, PCl_5)
4	1	 **Distorted tetrahedral**  (example, SF_4)
3	2	 **T-shaped**  (example, ClF_3)
2	3	 **Linear** (example, I_3^-)

Figure 10.7 | **Molecular shapes with five domains around the central atom.** Four different molecular structures are possible, depending on the number of nonbonding domains around the central atom *M*.

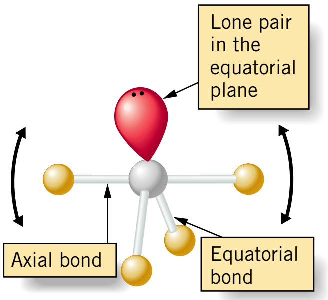


Figure 10.8 | **This distorted tetrahedron is sometimes described as a *seesaw* *structure*.** The origin of this description can be seen if we tip the structure over so it stands on the two atoms in the equatorial plane, with the nonbonding domain pointing up.

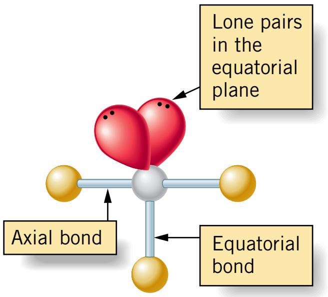


Figure 10.9 | **A molecule with two nonbonding domains in the equatorial plane of the trigonal bipyramid.** When tipped over, the molecule looks like a T, so it is called **T-shaped.**

Figure 10.7 shows the kinds of geometries that we find for different numbers of nonbonding domains in the trigonal bipyramid. When there is only one nonbonding domain, as in SF_4, the structure is described as a **distorted tetrahedron** or **seesaw** in which the central atom lies along one edge of a four-sided figure (Figures 10.7 and 10.8). With two nonbonding domains in the equatorial plane, the molecule is **T-shaped** (shaped like the letter T, Figure 10.9), and when there are three nonbonding domains in the equatorial plane, the molecule is **linear**.

Molecules with Six Electron Domains around the Central Atom

Finally, we come to molecules or ions that have six domains around the central atom. When all are in bonds, as in SF_6, the molecule is octahedral (Figure 10.4). When one nonbonding domain is present, the molecule or ion has the shape of a **square pyramid,** and when two nonbonding domains are present, they take positions on opposite sides of the nucleus and the molecule or ion has a **square planar** structure. These shapes are shown in Figure 10.10.

■ No common molecule or ion with six electron domains around the central atom has more than two nonbonding domains.

Steps in Using the VSEPR Model to Determine Molecular Shape

Now that we've seen how nonbonding and bonding domains influence molecular shape we can develop a strategy for applying the VSEPR model. In following this strategy it will be to your advantage to learn to sketch the five basic geometries (linear, planar triangular, tetrahedral, trigonal bipyramidal, and octahedral).

TOOLS Applying VSEPR theory

Determining Molecular Shape Using the VSEPR Model

Step 1. Use the procedure in Figure 9.12 to construct the Lewis formula for the molecule or ion.

Step 2. Count the total number of electron domains (bonding plus nonbonding).

Step 3. Using the result from Step 2, select the basic geometry upon which the shape of the molecule is based. [Make a drawing that shows the location of the central atom and the directions in which the domains (both bonding and nonbonding) are oriented.]

Step 4. Add the appropriate number of atoms to the bonding domains.

Step 5. If there are any nonbonding domains, ignore them and use the arrangement of atoms around the central atom to obtain the description of the molecular shape, as shown in Figures 10.5, 10.7, and 10.10.

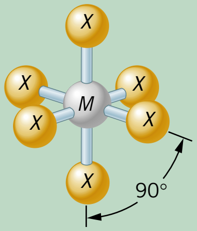
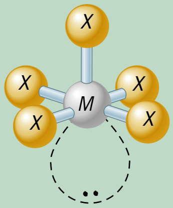
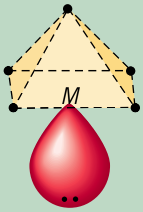
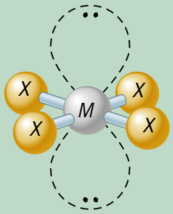
Number of Bonding Domains	Number of Nonbonding Domains	Structure	
6	0		**Octahedral** (example, SF_6) All bond angles are 90°.
5	1		**Square pyramidal**  (example, BrF_5)
4	2		**Square planar** (example, XeF_4)

Figure 10.10 | **Molecular shapes with six domains around the central atom.** Although more are theoretically possible, only three different molecular shapes are observed, depending on the number of nonbonding domains around the central atom.

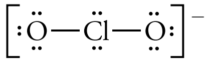
Example 10.2
Predicting the Shapes of Molecules and Ions

Do we expect the ClO_2^- ion to be linear?

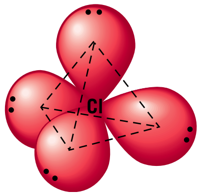
■ **Analysis:** This is a pretty straightforward application of the VSEPR model.

■ **Assembling the Tools:** The strategy described above for applying the VSEPR model as a tool first requires construction of the Lewis formula. The tool for this is Figure 9.12 on page 384.

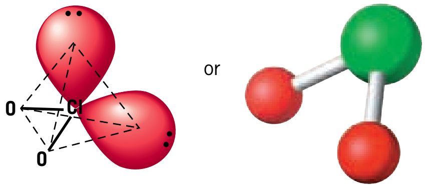
■ **Solution:** Following the usual procedure described in Figure 9.12, the Lewis structure for ClO_2^- is



Next, we count bonding and nonbonding domains around the central atom. There are four domains around the chlorine: two bonding and two nonbonding. Four domains (according to the theory) are always arranged tetrahedrally. This gives



Now we add the two oxygens, as shown below on the left. It doesn't matter which locations in the tetrahedron we choose because all the bond angles are equal. Below, on the right, we see how the structure of the ion looks when we ignore the lone pairs.



Notice that the O—Cl—O angle is less than 180°, so we predict the ion to be nonlinear (or bent or V-shaped).

■ For a molecule with three atoms, there are only two ways they can be arranged: either in a straight line (linear) or in a nonlinear arrangement.

■ **Is the Answer Reasonable?** Here are questions we have to answer to check our work. First, have we drawn the Lewis structure correctly? Have we counted the domains correctly? Have we selected the correct orientation of the domains? And finally, have we correctly described the structure obtained by adding the two oxygen atoms? Our answer to each of these questions is "Yes," so we can be confident our answer is right.

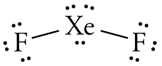
Example 10.3
Predicting the Shapes of Molecules and Ions

Xenon is one of the noble gases, and is generally quite unreactive. In fact, it was long believed that all the noble gases were totally unable to form compounds. It came as quite a surprise, therefore, when it was discovered that some compounds could be made. One of these is xenon difluoride. What would you expect the geometry of xenon difluoride to be—linear or nonlinear?

■ Analysis: This problem is similar to previous examples we've worked out. The first step will be to correctly write the formula of the compound. Then we can construct the Lewis formula, from which we can derive the shape of the molecule by applying the VSEPR model.

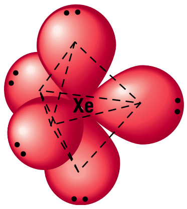
■ Assembling the Tools: First, we need the rules of nomenclature from Chapter 3 to obtain the formula of xenon tetrafluoride, which is XeF_2. We then follow the procedure in Figure 9.12 to construct the Lewis formula. From here, we follow the strategy for applying the VSEPR model.

■ Solution: The outer shell of xenon, of course, has a noble gas configuration, which contains 8 electrons. Each fluorine has 7 valence electrons. Using this information we obtain the following Lewis structure for XeF_2.

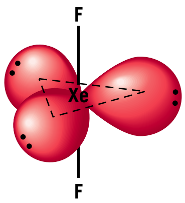


$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}-\underset{\cdot\cdot}{\overset{\cdot\cdot\;\cdot\cdot}{Xe}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

Next we count domains around xenon; there are five of them, three nonbonding and two bonding. When there are five domains, they are arranged in a trigonal bipyramid.



Now we must add the fluorine atoms. In a trigonal bipyramid, the nonbonding domains always occur in the equatorial plane through the center, so the fluorines go on the top and bottom. This gives



The three atoms, F—Xe—F, are arranged in a straight line, so the molecule is linear.

■ Is the Answer Reasonable? Is the Lewis structure correct? Yes. Have we selected the correct basic geometry? Yes. Have we attached the F atoms to the Xe correctly? Yes. All is in order, so the answer is correct.

Example 10.4
Predicting the Shapes of Molecules and Ions

The Lewis structure for the very poisonous gas hydrogen cyanide, HCN, is

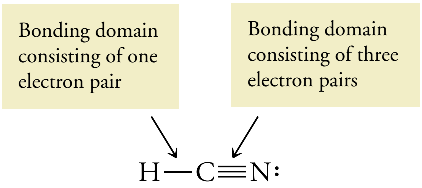
$$H-C\equiv N:$$

Is the HCN molecule linear or nonlinear?

■ Analysis: We already have the Lewis structure, so we count electron domains and proceed as before. The critical link in this problem is remembering that a bonding domain connects one atom to the central atom and that *all the electron pairs in a given bond belong to the same bonding domain.*

■ **Assembling the Tools:** As before, the tool required is the strategy for applying the VSEPR model.

■ **Solution:** There are two bonding domains around the carbon: one for the triple bond with nitrogen and one for the single bond with hydrogen.


Bonding domain consisting of one electron pair
Bonding domain consisting of three electron pairs
H—C≡N:

Therefore, we expect the two bonds to locate themselves 180° apart, yielding a linear HCN molecule.

■ **Is the Answer Reasonable?** Have we correctly counted bonding domains? Yes. We can expect our answer to be correct.

Practice Exercises

10.3 | The first known compound of the noble gas argon is HArF. What shape is expected for the HArF molecule? (*Hint:* Remember that argon is a noble gas with 8 electrons in its valence shell.)

10.4 | What shape is expected for the IBr_2^- ion?

10.5 | What shape is expected for the RnF_4 molecule?

10.6 | Predict the shapes of SO_3^{2-}, $PbCl_4$, XeO_4, and OF_2.

10.3 | Molecular Structure and Dipole Moments

■ Any molecule composed of just two atoms that differ in electronegativity must be polar because the bond is polar.

For a diatomic molecule, the dipole moment is determined solely by the polarity of the bond between the two atoms. Thus, the HCl molecule has a nonzero dipole moment because the H—Cl bond is polar, whereas H_2 has a dipole moment equal to zero because the H—H bond is nonpolar.

For a molecule containing three or more atoms, each polar bond has its own **bond dipole,** which contributes to the overall dipole moment of the molecule. This happens because the bond dipoles have *vector properties*, with both direction and magnitude. In a molecule, the bond dipoles add as vectors do.

Figure 10.11 shows three molecules in which vector addition of the bond dipoles leads to complete cancellation and dipole moments equal to zero. In the figure, the bond dipoles

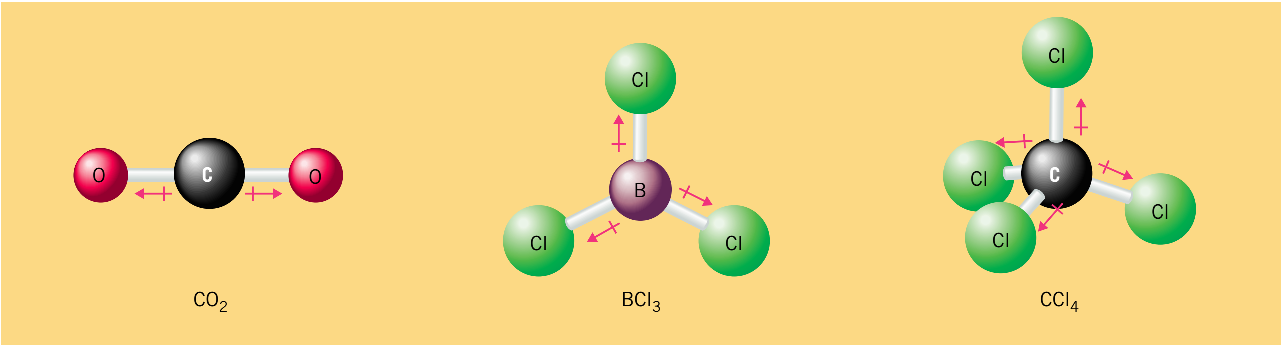
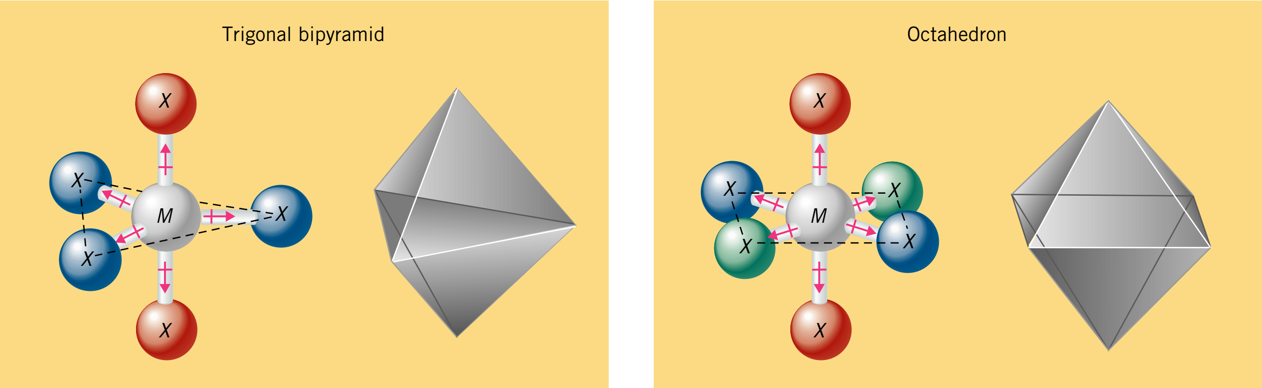


Figure 10.11 | **Molecular shape and its effect on the dipole moment.** Even though these molecules have polar bonds, vector addition of their bond dipoles leads to dipole moments of zero, which means the molecules are nonpolar.



(*a*) (*b*)

Figure 10.12 | **Cancellation of bond dipoles in symmetric trigonal bipyramidal and octahedral molecules.** In this figure, the colors of atoms are used to identify different sets of atoms within the molecule. (*a*) A trigonal bipyramidal molecule, MX_5, in which the central atom M is bonded to five identical atoms X. The set of three bond dipoles in the triangular plane in the center (in blue) cancel, as do the linear set of dipoles (red). Overall, the molecule is nonpolar. (*b*) An octahedral molecule MX_6 in which the central atom is bonded to six identical atoms. This molecule contains three linear sets of bond dipoles (red, blue, and green). Cancellation occurs for each set, so the molecule is nonpolar overall.

are indicated by arrows with plus signs at one end, $\mapsto$, to show which end of the dipole is positive. On the left is the linear CO_2 molecule in which both C—O bonds are identical. The individual bond dipoles have the same magnitude, but they point in opposite directions. Vector addition leads to cancellation and a net dipole moment of zero, just as adding numbers such as $+5$ and -5 gives a sum of zero. Because the dipole moment is zero, the CO_2 molecule is nonpolar. Although it isn't so easy to visualize, the same thing also happens in BCl_3 and CCl_4. In each of these molecules, the influence of one bond dipole is canceled by the effects of the others, which causes the molecules to have net dipole moments of zero. As a result, BCl_3 and CCl_4 are **nonpolar molecules**.

Although the molecules in Figure 10.11 are nonpolar, the fact that they contain nonzero bond dipoles means that the atoms carry some partial positive or negative charge. In CO_2, for example, the carbon carries a partial positive charge and an equal negative charge is divided between the two oxygen atoms. Similarly, in BCl_3 and CCl_4, the central atoms have partial positive charges and the chlorine atoms have partial negative charges.

Perhaps you've noticed that the structures of the molecules in Figure 10.11 correspond to three of the basic shapes that we used to derive the shapes of molecules. Molecules with the remaining two structures, trigonal bipyramidal and octahedral, also are nonpolar if all the atoms attached to the central atom are the same. All of the basic shapes are "balanced," or **symmetric**,[1] if all of the domains and groups attached to them are identical. Examples are shown in Figure 10.12. The trigonal bipyramidal structure can be viewed as a planar triangular set of atoms (shown in blue) plus a pair of atoms arranged linearly (shown in red). All the bond dipoles in the planar triangle cancel, as do the two dipoles of the bonds arranged linearly, so the molecule is nonpolar overall. Similarly, we can look at the octahedral molecule as consisting of three linear sets of bond dipoles. Cancellation of bond dipoles occurs in each set, so overall the octahedral molecule is also nonpolar.

---

[1] Symmetry is a more complex subject than we present it here. When we describe the symmetry properties of a molecule, we are specifying the various ways the molecule can be turned and otherwise manipulated while leaving the molecule looking exactly as it appeared before the manipulation. For example, imagine the BCl_3 molecule in Figure 10.11 being rotated 120° around an axis perpendicular to the page, that passes through the B atom. Performing this rotation leaves the molecule looking just as it did before the rotation. This rotation axis is a symmetry property of BCl_3.

Intuitively, we can recognize when an object possesses symmetry elements such as rotation axes (as well as other symmetry properties we haven't mentioned). Comparing objects, we can usually tell when one is more symmetric than another, and in our discussions in this chapter we rely on this qualitative sense of symmetry.

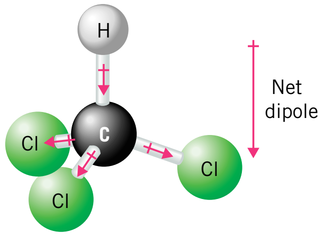


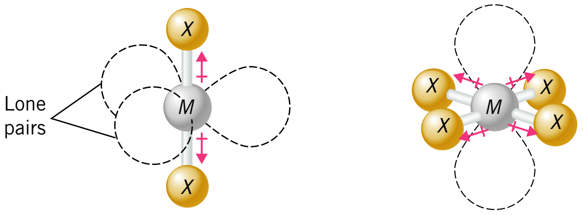
Figure 10.13 | **Bond dipoles in the chloroform molecule, $CHCl_3$.** Because C is slightly more electronegative than H, the C—H bond dipole points toward the carbon. The small C—H bond dipole actually adds to the effects of the C—Cl bond dipoles. All the bond dipoles are additive, and this causes $CHCl_3$ to be a polar molecule.

■ The lone pairs also influence the polarity of a molecule, but we will not explore this any further here.

*If all the atoms attached to the central atom are **not** the same, or if there are lone pairs in the valence shell of the central atom, the molecule is **usually** polar.* For example, in $CHCl_3$, one of the atoms in the tetrahedral structure is different from the others. The C—H bond is less polar than the C—Cl bonds, and the bond dipoles do not cancel (Figure 10.13). An "unbalanced" structure such as this is said to be **dissymmetric.**

Two familiar molecules that have lone pairs in the valence shells of their central atoms are shown in Figure 10.14. In these molecules the bond dipoles are oriented in such a way that their effects do not cancel. In water, for example, each bond dipole points partially in the same direction, toward the oxygen atom. As a result, the bond dipoles partially add to give a net dipole moment for the molecule. The same thing happens in ammonia, where three bond dipoles point partially in the same direction and add to give a polar NH_3 molecule.

Not every structure that contains nonbonding domains on the central atom produces polar molecules. The following are two exceptions.



No net dipole

In the first case, we have a pair of bond dipoles arranged linearly, just as they are in CO_2. In the second, the bonded atoms lie at the corners of a square, which can be viewed as two linear sets of bond dipoles. *If the atoms attached to the central atom are the same and are arranged linearly*, cancellation of bond dipoles occurs and produces nonpolar molecules. This means that molecules such as linear XeF_2 and square planar XeF_4 are nonpolar.

TOOLS

Molecular shape and molecular polarity

In Summary

- A molecule will be nonpolar if (a) the bonds are nonpolar or (b) there are no lone pairs in the valence shell of the central atom and all the atoms attached to the central atom are the same.
- A molecule in which the central atom has lone pairs of electrons will usually be polar, with the two exceptions described above in which the attached atoms are arranged so that their bond dipoles cancel.

On the basis of the preceding discussions, let's see how we apply these ideas to predict whether molecules are expected to be polar or nonpolar.

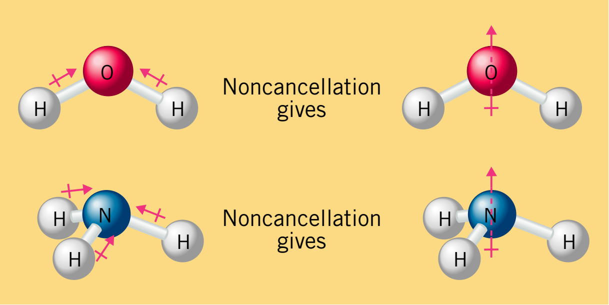


Figure 10.14 | **Dipole moments in water and ammonia.** Each of these molecules contains nonbonding domains in the valence shell of the central atoms and has a net dipole moment. When nonbonding domains occur on the central atom, the bond dipoles usually do not cancel, and polar molecules result.

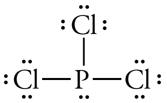
Example 10.5
Predicting Molecular Polarity

Do we expect the phosphorus trichloride molecule to be polar or nonpolar?

Analysis: Answering this seemingly simple question actually requires answering a number of questions. Are the bonds in the molecule polar or nonpolar? If they are polar, do the bond dipoles cancel? To answer that question, we need to know the shape of the molecule and whether there are lone pairs around the central atom. To find the shape of the molecule we have to construct the Lewis structure and apply the VSEPR model.

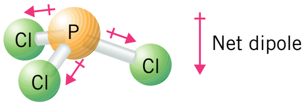
Assembling the Tools: First, we need to apply the nomenclature rules from Chapter 3 to convert the name of the compound into a chemical formula, which gives PCl_3. Next, we'll use electronegativities as a tool to determine whether the bonds in the molecule are polar. If they're not, the molecule will be nonpolar regardless of its structure. If the bonds are polar, we then need to determine the molecular structure. Our tools will be the procedure for drawing the Lewis structure and the VSEPR model. On the basis of the molecular structure, we can then decide whether the bond dipoles cancel.

Solution: The electronegativities of the atoms (P = 2.1, Cl = 2.9) tell us that the individual P—Cl bonds will be polar. Therefore, to predict whether or not the molecule is polar, we need to know its shape. First, we draw the Lewis structure following our usual procedure.



$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ | \\ :\underset{..}{\ddot{\mathrm{Cl}}}-\underset{..}{\mathrm{P}}-\underset{..}{\ddot{\mathrm{Cl}}}: \end{array}$$

There are four domains around the phosphorus, so they should be arranged tetrahedrally. This means that the PCl_3 molecule should have a trigonal pyramidal shape, as shown in the margin. Because of the structure, the bond dipoles do not cancel, and we expect the molecule to be polar.



Is the Answer Reasonable? There's not much to do here except to carefully check the Lewis structure to be sure it's correct and to check that we've applied the VSEPR theory correctly.

Example 10.6
Predicting Molecular Polarity

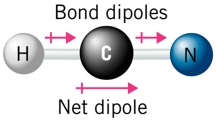
Would you expect the molecule HCN to be polar or nonpolar?

Analysis and Tools: Our analysis proceeds as in Example 10.5, so we will apply the same tools.

Solution: To begin, we have polar bonds, because carbon is slightly more electronegative than hydrogen and nitrogen is slightly more electronegative than carbon. The Lewis structure of HCN is

$$\mathrm{H}-\mathrm{C}\equiv\mathrm{N}:$$

There are two domains around the central carbon atom, so we expect a linear shape. However, the two bond dipoles do not cancel. One reason is that they are not of equal magnitude, which we know because the difference in electronegativity between C and H is 0.4, whereas the difference in electronegativity between C and N is 0.6. The other



reason is because both bond dipoles point in the same direction, from the atom of low electronegativity to the one of high electronegativity. This is illustrated in the margin. Notice that the bond dipoles combine by vector addition to give a net dipole moment for the molecule that is larger than either of the individual bond dipoles. As a result, HCN is a polar molecule.

■ **Is the Answer Reasonable?** As in the preceding example, we can check that we've obtained the correct Lewis structure and applied the VSEPR theory correctly, which we have. We can also check to see whether we've used the electronegativities to reach the right conclusions, which we have. We can be confident in our conclusions.

Practice Exercises

10.7 | Is the sulfur tetrafluoride molecule polar or nonpolar? (*Hint:* Use the VSEPR model to sketch the shape of the molecule.)

10.8 | Which of the following molecules would you expect to be polar? (a) TeF_6, (b) SeO_2, (c) BrCl, (d) AsH_3, (e) CF_2Cl_2

10.4 | Valence Bond Theory

So far we have described the bonding in molecules using Lewis structures. Lewis structures, however, tell us nothing about *why* covalent bonds are formed or *how* electrons manage to be shared between atoms. Nor does the VSEPR model explain *why* electrons group themselves into domains as they do. Thus, we must look beyond these simple models to understand more fully the covalent bond and the factors that determine molecular geometry.

There are fundamentally two theories of covalent bonding that have evolved based on quantum theory: the **valence bond theory** (or **VB theory**, for short) and the **molecular orbital theory (MO theory)**. They differ principally in the way they construct a theoretical model of the bonding in a molecule. The valence bond theory imagines individual atoms, each with its own orbitals and electrons, coming together to form the covalent bonds of the molecule. The molecular orbital theory doesn't concern itself with *how* the molecule is formed. It just views a molecule as a collection of positively charged nuclei surrounded in some way by electrons that occupy a set of *molecular orbitals*, in much the same way that the electrons in an atom occupy *atomic orbitals*. (In a sense, MO theory would look at an atom as if it were a special case—a molecule having only one positive center, instead of many.)

Bond Formation by Orbital Overlap

TOOLS

VB criteria for bond formation

According to VB theory, *a bond between two atoms is formed when* ***two electrons*** *with their* ***spins paired*** *are shared by two* ***overlapping*** *atomic orbitals, one orbital from each of the atoms joined by the bond.* By **overlap of orbitals** we mean that portions of two atomic orbitals from different atoms share the same space.[2]

An important part of the theory, as suggested by the bold italic type above, is that only *one* pair of electrons, with paired spins, can be shared by two overlapping orbitals. This electron pair becomes concentrated in the region of overlap and helps "cement" the nuclei together, so the amount that the potential energy is lowered when the bond is formed is determined in part by the extent to which the orbitals overlap. Therefore, *atoms tend to position themselves so that the maximum amount of orbital overlap occurs because this yields the minimum potential energy and therefore the strongest bonds.*

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[2] The concept of orbital overlap is actually more complicated than this and requires the application of quantum theory. For our purposes, the current definition will suffice.

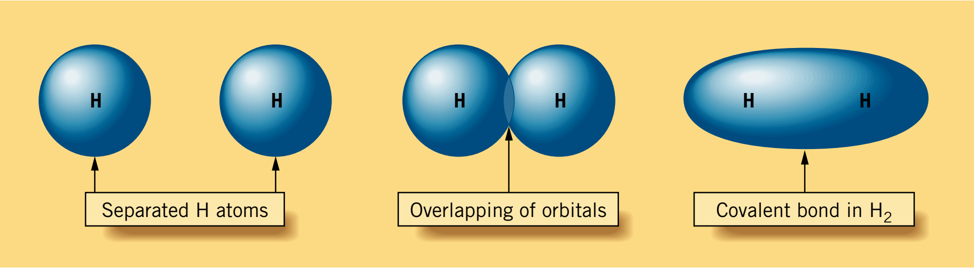


Figure 10.15 | **The formation of the hydrogen molecule according to valence bond theory.**

The way VB theory views the formation of a hydrogen molecule is shown in Figure 10.15. As the two atoms approach each other, their 1*s* orbitals begin to overlap and merge as the electron pair spreads out over both orbitals, thereby giving the H—H bond. The description of the bond in H_2 provided by VB theory is essentially the same as that discussed in Chapter 9.

Now let's look at the HF molecule, which is a bit more complex than H_2. Following the usual rules we can write its Lewis structure as

$$\mathrm{H{-}\ddot{\underset{\cdot\cdot}{F}}\!:}$$

and we can diagram the formation of the bond as

$$\mathrm{H\cdot + \cdot\ddot{\underset{\cdot\cdot}{F}}\!: \longrightarrow H{-}\ddot{\underset{\cdot\cdot}{F}}\!:}$$

Our Lewis symbols suggest that the H—F bond is formed by the pairing of electrons, one from hydrogen and one from fluorine. To explain this according to VB theory, we must have two half-filled orbitals, one from each atom, that can be joined by overlap. (They must be half-filled, because we cannot place more than two electrons into the bond.) To see clearly what must happen, it is best to look at the orbital diagrams of the valence shells of hydrogen and fluorine.

H	(↑)	
	1*s*	
F	(↑↓)	(↑↓)(↑↓)(↑)
	2*s*	2*p*

The requirements for bond formation are met by overlapping the half-filled 1*s* orbital of hydrogen with the half-filled 2*p* orbital of fluorine; there are then two orbitals plus two electrons whose spins can adjust so they are paired. The formation of the bond is illustrated in Figure 10.16.

The overlap of orbitals provides a means for sharing electrons, thereby allowing each atom to complete its valence shell. It is sometimes convenient to indicate this using orbital

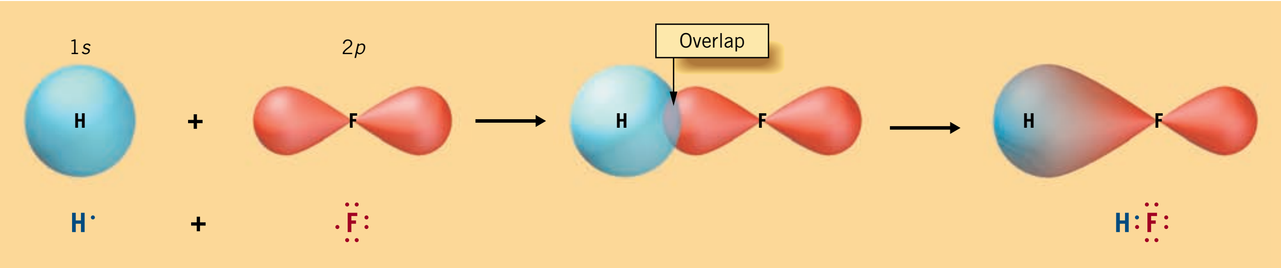


Figure 10.16 | **The formation of the hydrogen fluoride molecule according to valence bond theory.** For clarity, only the half-filled 2*p* orbital of fluorine is shown. The other 2*p* orbitals of fluorine are filled and cannot participate in bonding.

diagrams. For example, the diagram below shows how the fluorine atom completes its 2*p* subshell by acquiring a share of an electron from hydrogen.

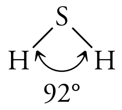
F (in HF) (↑↓) (↑↓)(↑↓)(↑↓) (Colored arrow is the H electron.)
2*s* 2*p*

Notice that in both the Lewis and VB descriptions of the formation of the H—F bond, the atoms' valence shells are completed.

Overlap of Atomic Orbitals and Molecular Shapes

■ H_2S is the compound that gives rotten eggs their foul odor.

Let's look now at a more complex molecule, hydrogen sulfide, H_2S. Experiments have shown that it is a nonlinear molecule in which the H—S—H bond angle is about 92°.



Using Lewis symbols, we would diagram the formation of H_2S as

$$2\text{H}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\cdot \longrightarrow \text{H}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}—\text{H}$$

■ If necessary, review the procedure for drawing orbital diagrams on page 329 in Chapter 8.

Our Lewis symbols suggest that each H—S bond is formed by the pairing of two electrons, one from H and one from S. Applying this to VB theory, each bond requires the overlap of two half-filled orbitals, one on H and one on S. Therefore, forming *two* H—S bonds in H_2S will require *two* half-filled orbitals on sulfur to form bonds to two separate H atoms. To clearly see what happens, let's look at the orbital diagrams of the valence shells of hydrogen and sulfur.

H (↑)
1*s*
S (↑↓) (↑↓)(↑)(↑)
3*s* 3*p*

Sulfur has two 3*p* orbitals that each contain only one electron. Each of these can overlap with the 1*s* orbital of a hydrogen atom, as shown in Figure 10.17. This overlap completes the 3*p* subshell of sulfur because each hydrogen provides one electron.

S (in H_2S) (↑↓) (↑↓)(↑↓)(↑↓) (Colored arrows are H electrons.)
3*s* 3*p*

■ In VB theory, two orbitals from different atoms never overlap simultaneously with opposite ends of the same *p* orbital.

In Figure 10.17, notice that when the 1*s* orbital of a hydrogen atom overlaps with a *p* orbital of sulfur, the best overlap occurs when the hydrogen atom lies along the axis of the

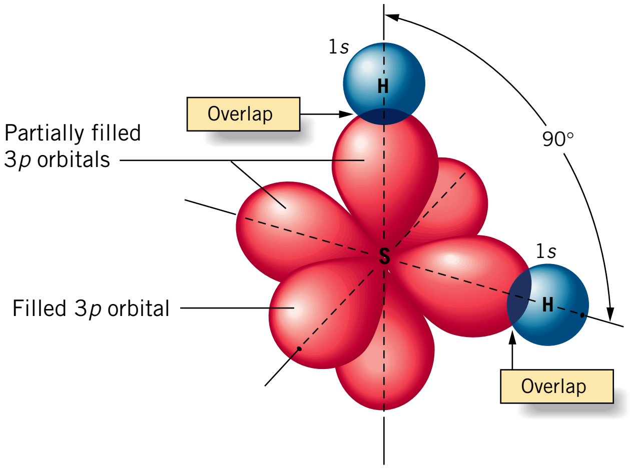


Figure 10.17 | **Bonding in H_2S.** We expect the hydrogen 1*s* orbitals to position themselves so that they can best overlap with the two partially filled 3*p* orbitals of sulfur, which gives a predicted bond angle of 90°. The experimentally measured bond angle of 92° is very close to the predicted angle.

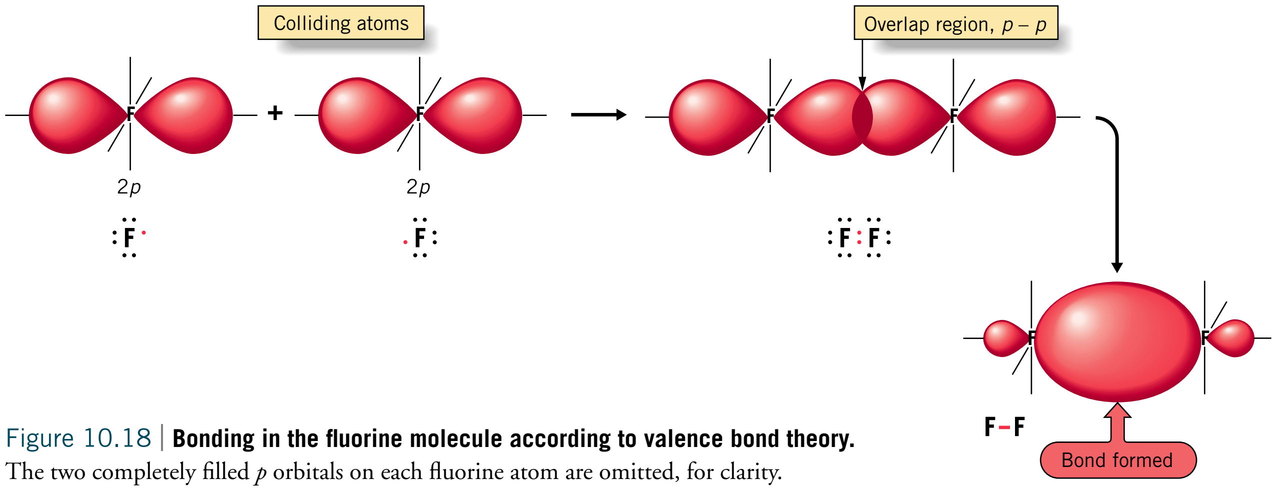


Figure 10.18 | **Bonding in the fluorine molecule according to valence bond theory.** The two completely filled *p* orbitals on each fluorine atom are omitted, for clarity.

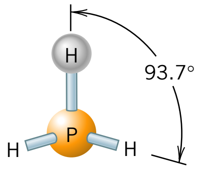
p orbital. Because *p* orbitals are oriented at 90° to each other, the H—S bonds are expected to be at this angle, too. Therefore, the predicted bond angle is 90°. This is very close to the actual bond angle of 92° found by experiment. Thus, the VB theory requirement for maximum overlap quite nicely explains the geometry of the hydrogen sulfide molecule. Also, notice that both the Lewis and VB descriptions of the formation of the H—S bonds account for the completion of the atoms' valence shells. Therefore, *a Lewis structure can be viewed, in a very qualitative sense, as a shorthand notation for the valence bond description of a molecule.*

Other kinds of orbital overlaps are also possible. For example, according to VB theory the bonding in the fluorine molecule, F_2, occurs by the overlap of two 2*p* orbitals, as shown in Figure 10.18. The formation of the other diatomic molecules of the halogens, all of which are held together by single bonds, could be similarly described.

Practice Exercises

10.9 | Use the principles of VB theory to explain the bonding in HCl. Give the orbital diagram for chlorine in the HCl molecule and indicate the orbital that shares the electron with one from hydrogen. Sketch the orbital overlap that gives rise to the H—Cl bond. (*Hint:* Remember that a half-filled orbital on each atom is required to form the covalent bond.)

10.10 | The phosphine molecule, PH_3, has a trigonal pyramidal shape with H—P—H bond angles equal to 93.7°, as shown in the margin. Give the orbital diagram for phosphorus in the PH_3 molecule and indicate the orbitals that share electrons with those from hydrogen. On a set of *xyz* coordinate axes, sketch the orbital overlaps that give rise to the P—H bonds.



10.5 | Hybrid Orbitals and Molecular Geometry

There are many molecules for which the simple VB theory described in Section 10.4 fails to account for the correct shape. For example, there are no simple atomic orbitals that are oriented so they point toward the corners of a tetrahedron, yet there are many tetrahedral molecules. Therefore, to explain the bonds in molecules such as CH_4 we must study the way atomic orbitals *of the same atom* mix with each other to produce new orbitals, called **hybrid atomic orbitals.**[3] The new orbitals have new shapes and new directional properties, and they can overlap to give structures with bond angles that match those found by experiment. It's important to realize that hybrid orbitals are part of the valence bond *theory.* They can't be directly observed in an experiment. We use them to describe molecular structures that have been determined experimentally.

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[3] Mathematically, hybrid orbitals are formed by the addition and subtraction of the wave functions for the basic atomic orbitals. This process produces a new set of wave functions corresponding to the hybrid orbitals. The hybrid orbital wave functions describe the shape and directional properties of the hybrid orbitals.

Hybrid Orbitals Formed from *s* and *p* Atomic Orbitals

Let's begin by studying what happens when we mix a 2*s* orbital with a 2*p* orbital to form a new set of two orbitals that we designate as ***sp* hybrid orbitals,** illustrated in Figure 10.19. First, notice that each has the same shape; each has one large lobe and another much smaller one. The large lobe extends farther from the nucleus than either the *s* or *p* orbital from which the hybrid was formed. This allows the hybrid orbital to overlap more effectively with an orbital on another atom when a bond is formed. As a result, hybrid orbitals form stronger, more stable, bonds than would be possible if just simple atomic orbitals were used.

■ In general, the greater the overlap of two orbitals, the stronger is the bond. At a given distance between nuclei, the greater "reach" of a hybrid orbital gives better overlap than either an *s* or a *p* orbital.

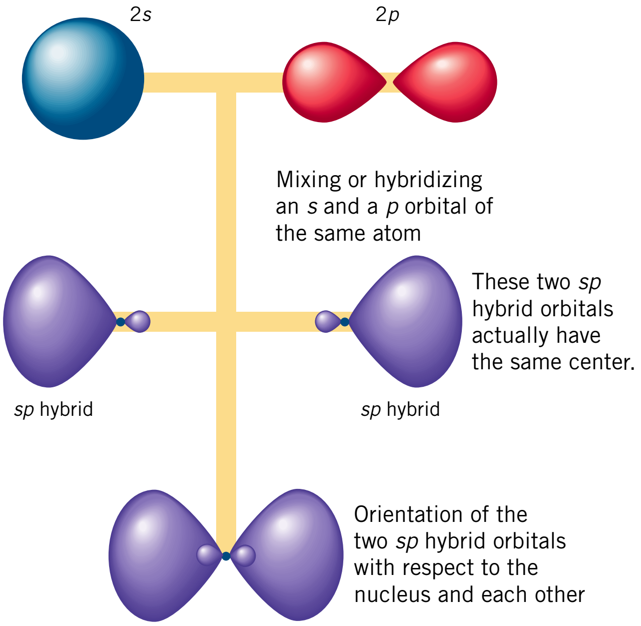
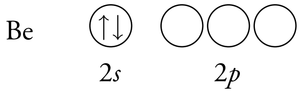

2*s*
2*p*
Mixing or hybridizing an *s* and a *p* orbital of the same atom
These two *sp* hybrid orbitals actually have the same center.
sp hybrid
sp hybrid
Orientation of the two *sp* hybrid orbitals with respect to the nucleus and each other

Figure 10.19 | **Formation of *sp* hybrid orbitals.** Mixing of 2*s* and 2*p* atomic orbitals produces a pair of *sp* hybrid orbitals. The large lobes of these orbitals have their axes pointing in opposite directions.

Another point to notice in Figure 10.19 is that the large lobes of the two *sp* hybrid orbitals point in opposite directions; that is, they are 180° apart. If bonds are formed by the overlap of these hybrids with orbitals of other atoms, the other atoms will occupy positions on opposite sides of this central atom. Let's look at a specific example—the linear beryllium hydride molecule, BeH_2, as it would be formed in the gas phase.[4]

The orbital diagram for the valence shell of beryllium is



Notice that the 2*s* orbital is filled and the three 2*p* orbitals are empty. For bonds to form at a 180° angle between beryllium and the two hydrogen atoms, two conditions must be met: (1) the two orbitals that beryllium uses to form the Be—H bonds must point in opposite directions, and (2) each of the beryllium orbitals must contain only one electron. In satisfying these requirements, the electrons of the beryllium atom become unpaired and the resulting half-filled *s* and *p* atomic orbitals become hybridized.

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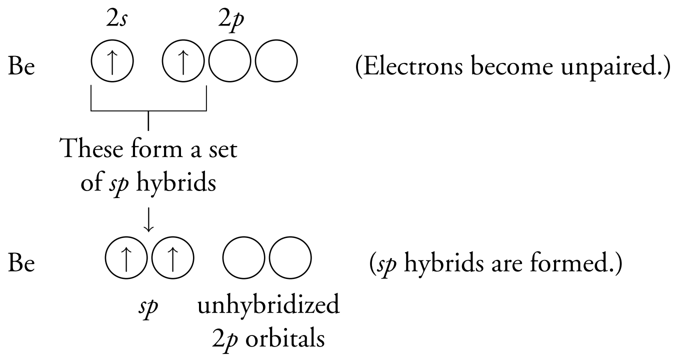
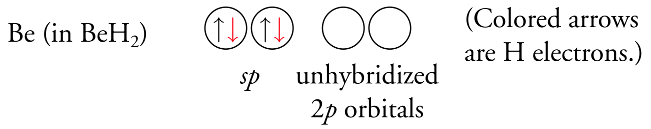
[4] In the solid state, BeH_2 has a complex structure not consisting of simple BeH_2 molecules.


2s
2p
Be
(Electrons become unpaired.)
These form a set of sp hybrids
Be
(sp hybrids are formed.)
sp
unhybridized 2p orbitals

Now the 1*s* orbitals of the hydrogen atoms can overlap with the *sp* hybrids of beryllium to form the bonds, as shown in Figure 10.20. Because the two *sp* hybrid orbitals of beryllium are identical in shape and energy, the two Be—H bonds are alike except for the directions in which they point, and we say that the bonds are *equivalent*. Since the bonds point in opposite directions, the linear geometry of the molecule is also explained. The orbital diagram for beryllium in this molecule is


Be (in BeH2)
(Colored arrows are H electrons.)
sp
unhybridized 2p orbitals

Even if we had not known the shape of the BeH_2 molecule, we could have obtained the same bonding picture by applying the VSEPR model first. The Lewis structure for BeH_2 is H:Be:H, with two bonding domains around the central atom, so the molecule is linear. Once the shape is known, we can apply the VB theory to explain the bonding in terms of orbital overlaps. Thus, the VB theory and VSEPR model complement each other well. The VSEPR model allows us to predict geometry in a simple way, and once the geometry is known, it is relatively easy to analyze the bonding in terms of VB theory.

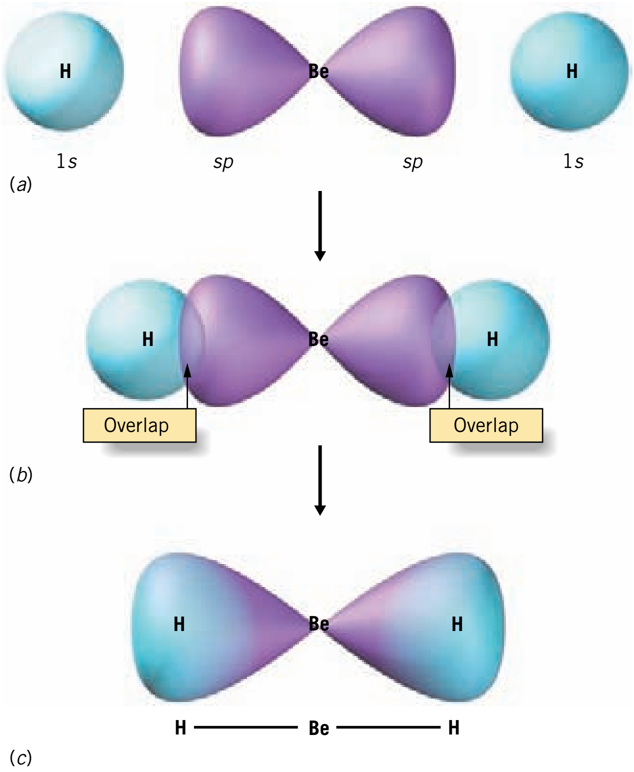
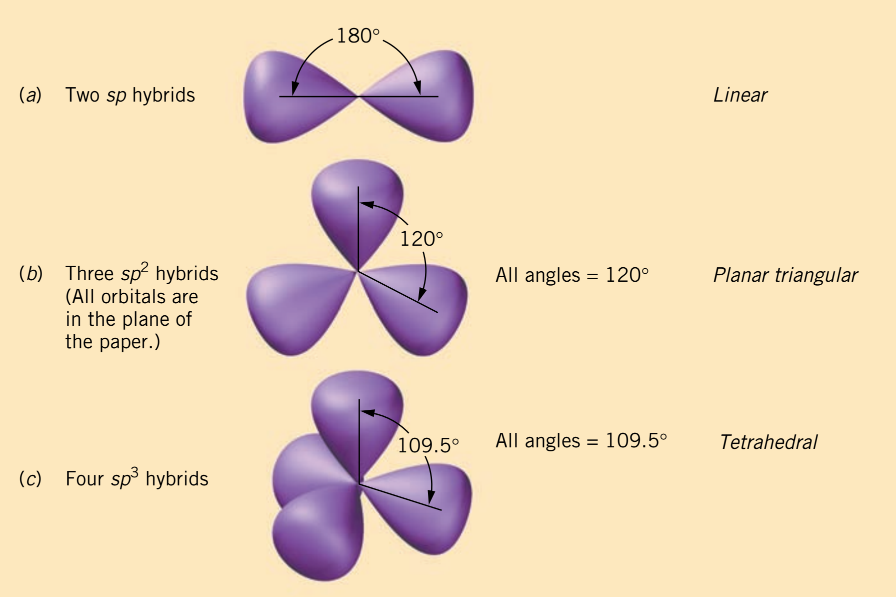

H
Be
H
1s
sp
sp
1s
(a)
H
Be
H
Overlap
Overlap
(b)
H
Be
H
H
Be
H
(c)

Figure 10.20 | **Bonding in BeH_2 according to valence bond theory.** Only the larger lobe of each *sp* hybrid orbital is shown. (*a*) The two hydrogen 1*s* orbitals approach the pair of *sp* hybrid orbitals of beryllium. (*b*) Overlap of the hydrogen 1*s* orbitals with the *sp* hybrid orbitals. (*c*) A representation of the distribution of electron density in the two Be—H bonds after they have been formed.

Figure 10.21 | **Directional properties of hybrid orbitals formed from *s* and *p* atomic orbitals.** (*a*) *sp* hybrid orbitals oriented at 180° to each other. (*b*) sp^2 hybrid orbitals formed from an *s* orbital and two *p* orbitals. The angle between them is 120°. (*c*) sp^3 hybrid orbitals formed from an *s* orbital and three *p* orbitals. The angle between any two of them is 109.5°.



TOOLS

Hybrid orbitals involving *s* and *p* atomic orbitals

In addition to *sp* hybrids, atomic *s* and *p* orbitals form two other kinds of hybrid orbitals. These are shown in Figure 10.21. In identifying hybrid orbitals, we specify which kinds of pure atomic orbitals, as well as the number of each, that are mixed to form the hybrids. Thus, hybrid orbitals labeled $\boldsymbol{sp^3}$ are formed by blending one *s* orbital and three *p* orbitals. *The total number of hybrid orbitals in a set is equal to the number of basic atomic orbitals used to form them.* Therefore, a set of sp^3 hybrids consists of four orbitals, whereas a set of $\boldsymbol{sp^2}$ orbitals consists of three orbitals.

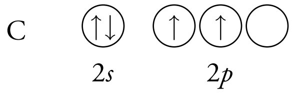
Example 10.7
Explaining Bonding with Hybrid Orbitals

Methane, CH_4, is a tetrahedral molecule. How is this explained in terms of valence bond theory?

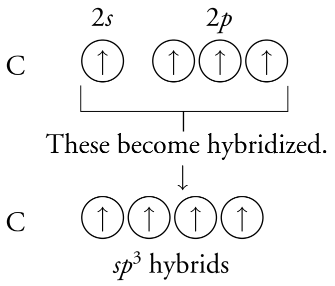
Analysis: No pure atomic orbitals have the correct orientations to form a tetrahedral molecule, so we expect hybrid orbitals will be used.

Assembling the Tools: Our tool is Figure 10.21, which permits us to select which hybrids are appropriate based on the geometry of the molecule. Then we can use the orbital diagram of carbon to follow the changes leading to bond formation.

Solution: The tetrahedral structure of the molecule suggests that sp^3 hybrid orbitals are involved in bonding. Let's examine the valence shell of carbon.

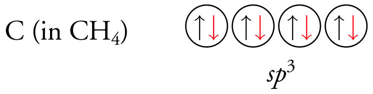


To form four C—H bonds, we need four half-filled orbitals. Unpairing the electrons in the 2*s* and moving one to the vacant 2*p* orbital satisfies this requirement. Then we can hybridize all the orbitals to give the desired sp^3 set.



(Electrons become unpaired.)

Then we form the four bonds to hydrogen 1*s* orbitals.



(Colored arrows are H electrons.)

This is illustrated in Figure 10.22.

Is the Answer Reasonable? The positions of the hydrogen atoms around the carbon give the correct tetrahedral shape for the molecule. The Lewis structure for CH_4 shows four bonding domains around the carbon atom, which is consistent with the idea of four sp^3 orbitals overlapping with hydrogen 1*s* orbitals to form four bonds.

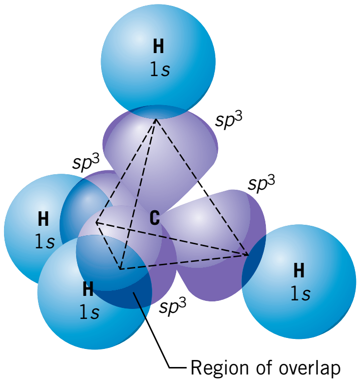


Figure 10.22 | **Formation of the bonds in methane.** Each bond results from the overlap of a hydrogen 1*s* orbital with an sp^3 hybrid orbital on the carbon atom.

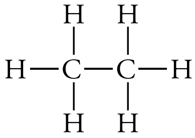
Practice Exercises

10.11 | The BF_3 molecule has a planar triangular shape. What kind of hybrid orbitals does boron use in this molecule? Use orbital diagrams to explain how the bonds are formed. (*Hint:* Which kind of hybrid orbitals are oriented correctly to give this molecular shape?)

10.12 | In the gas phase, beryllium fluoride exists as linear molecules. Which kind of hybrid orbitals does Be use in this compound? Use orbital diagrams to explain how the bonds are formed.

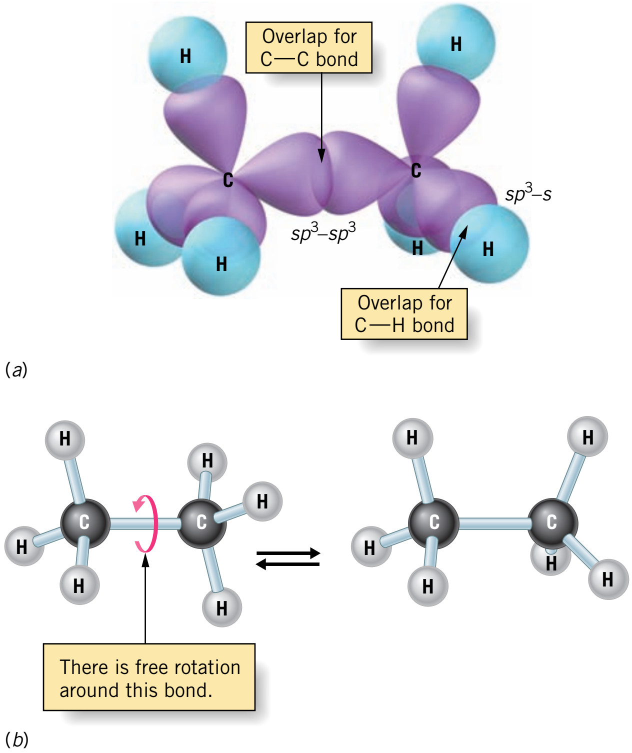
In methane, carbon forms four single bonds with hydrogen atoms by using sp^3 hybrid orbitals. In fact, carbon uses these same kinds of orbitals in all of its compounds in which it is bonded to four other atoms by single bonds. This makes the tetrahedral orientation of atoms around carbon one of the primary structural features of organic compounds, and organic chemists routinely think in terms of "tetrahedral carbon."

In the alkane series of hydrocarbons (compounds with the general formula $C_nH_{(2n+2)}$, page 92), carbon atoms are bonded to other carbon atoms. An example is ethane, C_2H_6.



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-H$$

In this molecule, the carbons are bonded together by the overlap of sp^3 hybrid orbitals (Figure 10.23). One of the most important characteristics of this bond is that the overlap of the orbitals in the C—C bond is hardly affected at all if one portion of the molecule rotates relative to the other around the bond axis. Such rotation, therefore, is said to occur freely and permits different possible relative orientations of the atoms in the molecule. These different relative orientations are called **conformations.** With complex molecules, the number of possible conformations is enormous. For example, Figure 10.24 illustrates three of the large number of possible conformations of the pentane molecule, C_5H_{12}, one of the low-molecular-weight organic compounds in gasoline.



Overlap for C—C bond

Overlap for C—H bond

There is free rotation around this bond.

Figure 10.23 | **The bonds in the ethane molecule.** (*a*) Overlap of orbitals. (*b*) The degree of overlap of the sp^3 orbitals in the carbon–carbon bond is not appreciably affected by the rotation of the two CH_3— groups relative to each other around the bond.

Using the VSEPR Model to Predict Hybridization

VSEPR model and hybridization

We've seen that if we know the structure of a molecule, we can make a reasonable guess as to the kind of hybrid orbitals that the central atom uses to form its bonds. Because the VSEPR model works so well in predicting geometry, we can use it to help us obtain VB descriptions of bonding. This is illustrated in the following example.

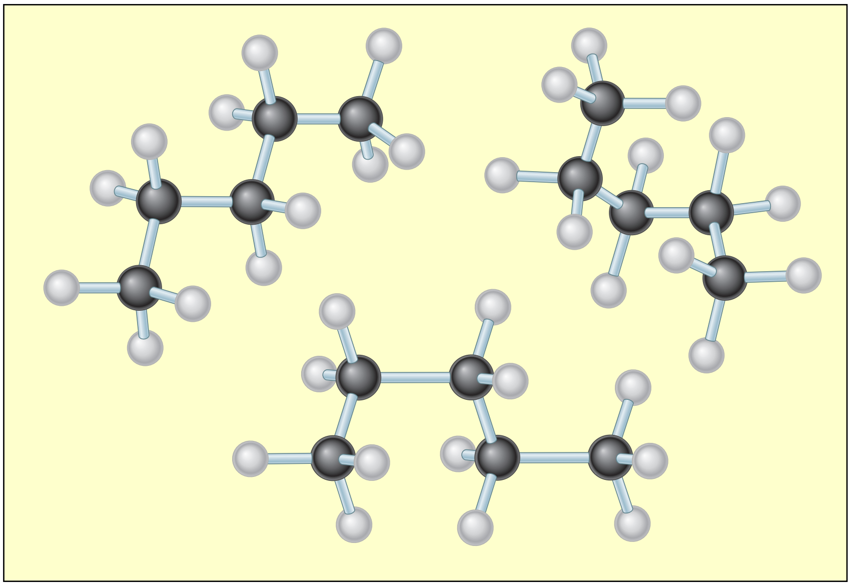


Figure 10.24 | **Three of the many conformations of the atoms in the pentane molecule, C_5H_{12}.** Free rotation around single bonds makes these different conformations possible.

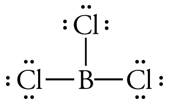
Example 10.8
Using the VSEPR Model to Predict Hybridization

Predict the shape of the boron trichloride molecule and describe the bonding in the molecule in terms of valence bond theory.

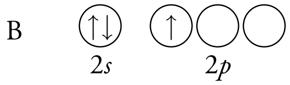
Analysis: This problem is similar to Example 10.7, except we're not given the shape of the molecule, which we need to select the kind of hybrid orbitals used by the central atom. The rules of nomenclature tell us the chemical formula is BCl_3. Based on the formula, we will write a Lewis structure for the molecule. This will permit us to determine its geometry by applying VSEPR theory. From the shape of the molecule, we can select the kind of hybrid orbitals used by the central atom and then use orbital diagrams to describe the bonding.

Assembling the Tools: Our tools will include the method for constructing Lewis structures and the VSEPR model. On the basis of the geometry predicted by the VSEPR model, we can select the appropriate hybrid orbitals from Figure 10.21.

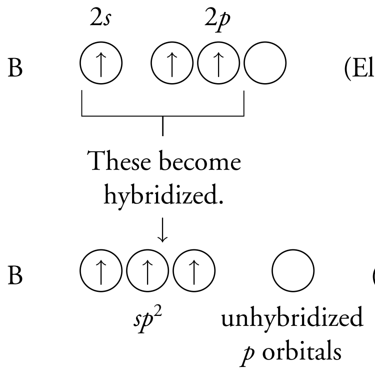
Solution: Keeping in mind that boron is an element that is permitted to have less than an octet in its valence shell and following the procedure described in Chapter 9, the Lewis structure for BCl_3 is



The VSEPR model tells us the molecule should be planar triangular, and referring to Figure 10.21, we find that the hybrid set that fits this structure is *sp*^{2}.



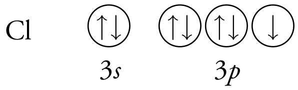
To form the three bonds to chlorine, boron needs three half-filled orbitals. These can be obtained by unpairing the electrons in the 2*s* orbital and placing one of them in the 2*p*. Then the 2*s* orbital and two of the 2*p* orbitals can be combined to give the set of three *sp*^{2} hybrids.



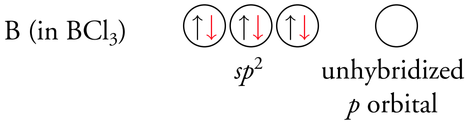
(Electrons become unpaired.)

(Orbitals are hybridized.)

Now let's look at the valence shell of chlorine.



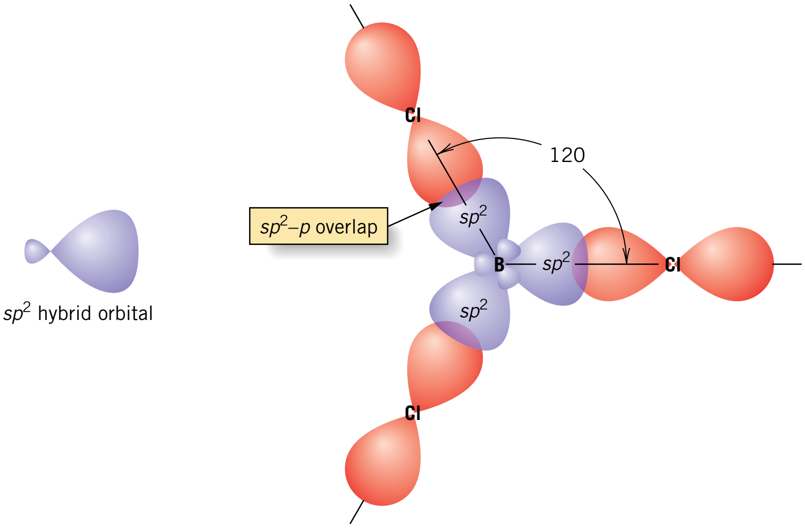
The half-filled 3*p* orbital of each chlorine atom can overlap with a hybrid *sp*^{2} orbital of boron to give three B—Cl bonds.



(Colored arrows are Cl electrons.)

Figure 10.25 illustrates the overlap of the orbitals to give the bonding in the molecule.

Figure 10.25 | **Description of the bonding in BCl_3.** Each B—Cl bond is formed by the overlap of a half-filled 3*p* orbital of a Cl atom with one of the sp^2 hybrid orbitals of boron. (For simplicity, only the half-filled 3*p* orbital of each Cl atom is shown.)



Is the Answer Reasonable? Notice that the arrangement of atoms yields a planar triangular molecule, in agreement with the structure predicted by the VSEPR model. This internal consistency is convincing evidence that we've answered the question correctly.

Practice Exercise

10.13 | What kind of hybrid orbitals are expected to be used by the central atom in SiH_4? Use orbital diagrams to describe the bonding in the molecule.

Hybrid Orbitals Formed from *s*, *p*, and *d* Orbitals

TOOLS

VSEPR theory and hybrid orbitals involving *s*, *p*, and *d* atomic orbitals

Earlier we saw that certain molecules have atoms that must violate the octet rule because they form more than four bonds. In these cases, the atom must reach beyond its *s* and *p* valence shell orbitals to form sufficient half-filled orbitals for bonding. This is because the *s* and *p* orbitals can be mixed to form a maximum of only four hybrid orbitals. When five or more hybrid orbitals are needed, *d* orbitals are brought into the mix. The two most common kinds of hybrid orbitals involving *d* orbitals are **sp^3d** and **sp^3d^2 hybrid orbitals.** Their directional properties are illustrated in Figure 10.26. Notice that the sp^3d hybrids point toward the corners of a trigonal bipyramid and the sp^3d^2 hybrids point toward the corners of an octahedron.

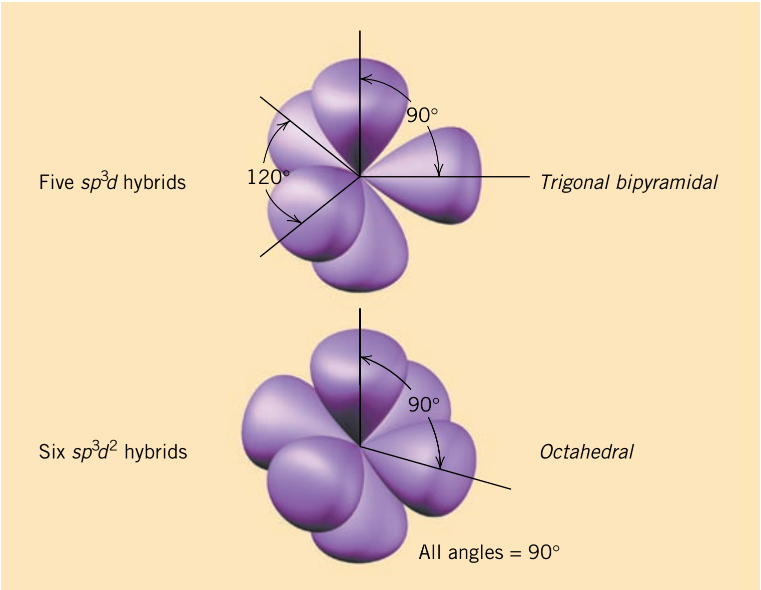


Figure 10.26 | **Orientations of hybrid orbitals that involve *d* orbitals.** (*a*) sp^3d hybrid orbitals formed from an *s* orbital, three *p* orbitals, and a *d* orbital. The orbitals point toward the vertices of a trigonal bipyramid. (*b*) sp^3d^2 hybrid orbitals formed from an *s* orbital, three *p* orbitals, and two *d* orbitals. The orbitals point toward the vertices of an octahedron.

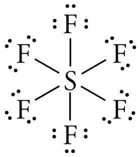
Example 10.9
Explaining Bonding with Hybrid Orbitals

Predict the shape of the sulfur hexafluoride molecule and describe the bonding in the molecule in terms of valence bond theory.

Analysis: The rules of nomenclature tell us the chemical formula is SF_6. Based on the formula, we will write a Lewis structure for the molecule. This will permit us to determine its geometry. From the shape of the molecule, we can select the kind of hybrid orbitals used by the central atom and then use orbital diagrams to describe the bonding.

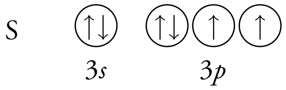
Assembling the Tools: Our tools will include the method for constructing Lewis structures and the VSEPR model. On the basis of the geometry predicted by the VSEPR model, we would then select the appropriate hybrid orbitals from Figures 10.21 or 10.26. However, the formula SF_6 tells us that we have more than four bonds in the molecules, so we can anticipate using Figure 10.26.

Solution: Following the procedure discussed earlier, the Lewis structure for SF_6 is



The VSEPR model tells us the molecule should be octahedral, and referring to Figure 10.26, we find that the hybrid set that fits this structure is sp^3d^2.

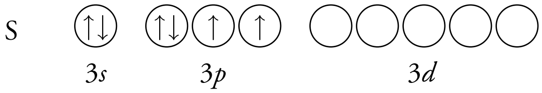
Now let's examine the valence shell of sulfur.



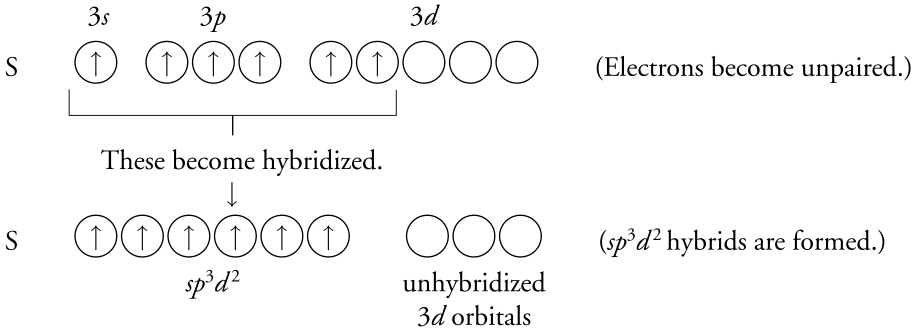
To form six bonds to fluorine atoms we need six half-filled orbitals, but we show only four orbitals altogether. However, sp^3d^2 orbitals tell us we need to look for *d* orbitals to include in the set of hybrids.

An isolated sulfur atom has electrons only in its 3*s* and 3*p* subshells, so these are the only subshells we usually show in the orbital diagram. But the third shell also has a *d* subshell, which is empty in a sulfur atom. Therefore, let's rewrite the orbital diagram to show the vacant 3*d* subshell.

Sulfur is able to exceed an octet because of the availability of *d* orbitals in its valence shell.



Unpairing all of the electrons to give six half-filled orbitals, followed by hybridization, gives the required set of half-filled sp^3d^2 orbitals (Figure 10.27).



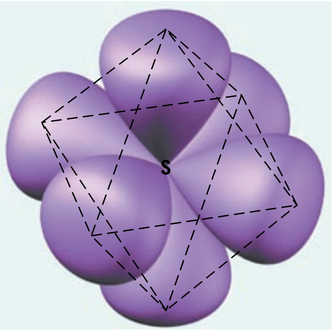
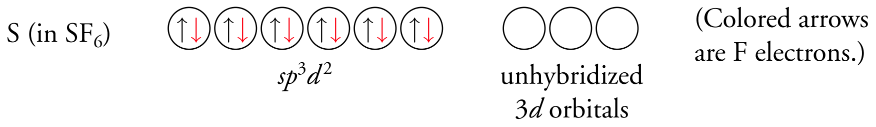


Figure 10.27 | **The sp^3d^2 hybrid orbitals of sulfur in SF_6.**

Finally, the six S—F bonds are formed by overlap of the half-filled 2*p* orbitals of the fluorine atoms with these half-filled sp^3d^2 hybrids.


S (in SF_6)
sp^3d^2
unhybridized
3*d* orbitals
(Colored arrows
are F electrons.)

Is the Answer Reasonable? Once again, the fact that all the parts fit together so well to account for the structure of SF_6 makes us feel that our explanation of the bonding is reasonable.

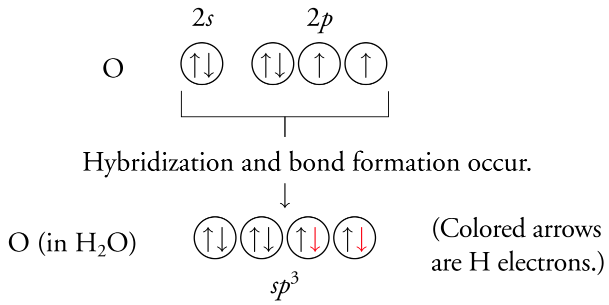
Practice Exercises

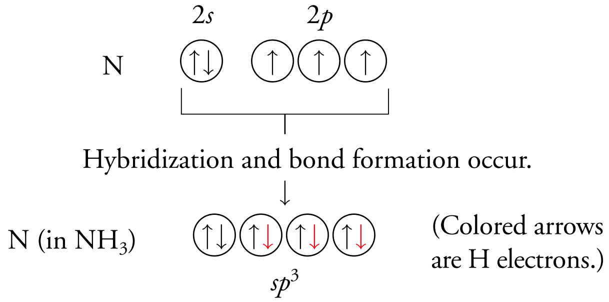
10.14 | What kind of hybrid orbitals are expected to be used by the central atom in PCl_5? (*Hint:* Which hybrid orbitals have the same geometry as the molecule?)

10.15 | Use the VSEPR model to predict the shape of the $AsCl_5$ molecule and then describe the bonding in the molecules using valence bond theory.

Molecules with Nonbonding Domains

Methane is a tetrahedral molecule with sp^3 hybridization of the orbitals of carbon and H—C—H bond angles that are each equal to 109.5°. In ammonia, NH_3, the H—N—H bond angles are 107°, and in water the H—O—H bond angle is 104.5°. Both NH_3 and H_2O have H—*X*—H bond angles that are close to the bond angles expected for a molecule whose central atom has sp^3 hybrids. The use of sp^3 hybrids by oxygen and nitrogen, therefore, is often used to explain the geometry of H_2O and NH_3.


2*s*
2*p*
O
Hybridization and bond formation occur.
O (in H_2O)
sp^3
(Colored arrows
are H electrons.)


2*s*
2*p*
N
Hybridization and bond formation occur.
N (in NH_3)
sp^3
(Colored arrows
are H electrons.)

According to these descriptions, not all of the hybrid orbitals of the central atom must be used for bonding. Lone pairs of electrons can be accommodated in them too, as illustrated in Figure 10.28. In fact, putting the lone pair on the nitrogen in an sp^3 hybrid orbital gives a geometry that agrees well with the experimentally determined structure of the ammonia molecule.

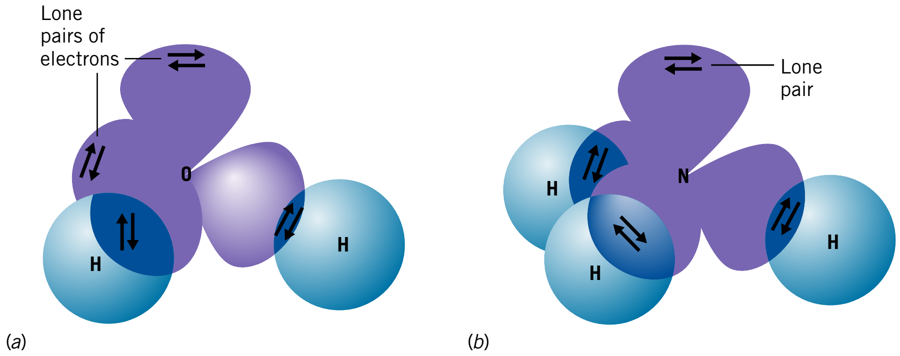


Figure 10.28 | **Hybrid orbitals can hold lone pairs of electrons.** (*a*) In water, two lone pairs on oxygen are held in sp^3 hybrid orbitals. (*b*) Ammonia has one lone pair in an sp^3 hybrid orbital.

Example 10.10

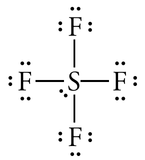
Explaining Bonding with Hybrid Orbitals

Use valence bond theory to explain the bonding in the SF_4 molecule.

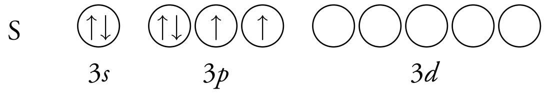
Analysis: In solving this problem we will follow the same steps as in Example 10.9: (1) Draw the Lewis structure, (2) predict the geometry of the molecule, (3) select the hybrid orbital set that fits the structure, and (4) construct orbital diagrams to explain the bonding.

Assembling the Tools: Our tools are the same as before. We apply our method for drawing Lewis structures from Chapter 9. We apply the VSEPR theory. We use Figures 10.21 or 10.26 to select the hybrid orbital set.

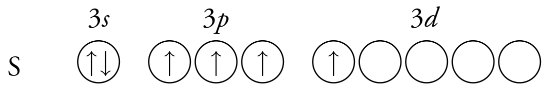
Solution: We begin by constructing the Lewis structure for the molecule.



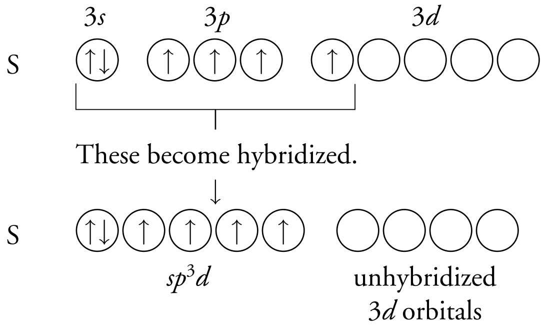
The VSEPR model predicts that the electron pairs around the sulfur should be in a trigonal bipyramidal arrangement, and the only hybrid set that fits this geometry is sp^3d (according to Figure 10.26). To see how the hybrid orbitals are formed, we look at the valence shell of sulfur, including the vacant 3*d* subshell.

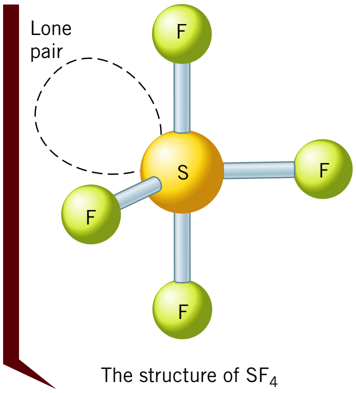


To form the four bonds to fluorine atoms, we need four half-filled orbitals, so we unpair the electrons in one of the filled orbitals. This gives



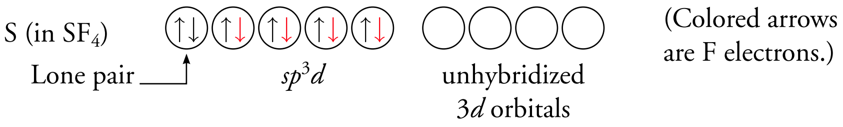
Next, we form the hybrid orbitals. In doing this, we use all the valence shell orbitals that have electrons in them.





The structure of SF_4

Now, four S—F bonds can be formed by overlap of half-filled 2*p* orbitals of fluorine with the sp^3d hybrid orbitals of sulfur to give the structure in the margin.



Is the Answer Reasonable? Counting electrons in the Lewis structure gives a total of 34, which is how many electrons are in the valence shells of one sulfur and four chlorine atoms, so the Lewis structure appears to be correct. The rest of the answer flows smoothly, so the bonding description appears to be reasonable. Notice that the VSEPR model even shows us which of the hybrid orbitals contains the lone pair.

Practice Exercises

10.16 | What kind of orbitals are used by Xe in the XeF_4 molecule? (*Hint:* An Xe atom has 8 valence electrons.)

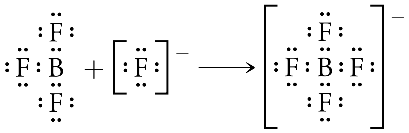
10.17 | What kind of hybrid orbitals would we expect the central atom to use for bonding in (a) PCl_3 and (b) $BrCl_3$?

Formation of Coordinate Covalent Bonds

In Section 9.8 we defined a coordinate covalent bond as one in which both of the shared electrons are provided by just one of the joined atoms. Such a bond is formed when boron trifluoride, BF_3, combines with an additional fluoride ion to form the tetrafluoroborate ion, BF_4^-.

$$BF_3 + F^- \longrightarrow \underset{\text{tetrafluoroborate ion}}{BF_4^-}$$

We can diagram this reaction as follows:



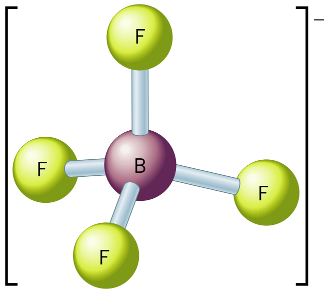
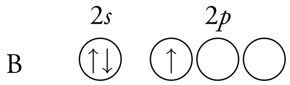


Figure 10.29 | **The tetrahedral structure of the BF_4^- ion.**

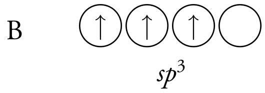
As we mentioned previously, the coordinate covalent bond is really no different from any other covalent bond once it has formed. The distinction is made *only* for bookkeeping purposes. One place where such bookkeeping is useful is in keeping track of the orbitals and electrons used when atoms bond together.

The VB theory requirements for bond formation—two overlapping orbitals sharing two paired electrons—can be satisfied in two ways. One, as we have already seen, is by the overlapping of two half-filled orbitals. This gives an "ordinary" covalent bond. The other is by overlapping one filled orbital with one empty orbital. The atom with the filled orbital donates the shared pair of electrons, and a coordinate covalent bond is formed.

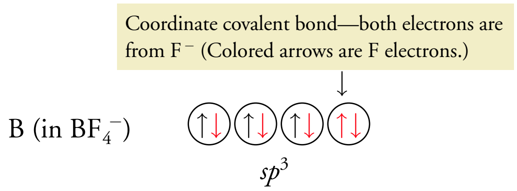
The structure of the BF_4^- ion, which the VSEPR model predicts to be tetrahedral (Figure 10.29), can be explained as follows. First, we examine the orbital diagram for boron.



To form four bonds, we need four hybrid orbitals arranged tetrahedrally around the boron, so we expect boron to use sp^3 hybrids. Notice that we spread the electrons out over the hybrid orbitals as much as possible.



Boron forms three ordinary covalent bonds with fluorine atoms plus one coordinate covalent bond with a fluoride ion.


Coordinate covalent bond—both electrons are from F$^-$ (Colored arrows are F electrons.)
B (in BF_4^-)
↑↓ ↑↓ ↑↓ ↑↓
sp^3

Practice Exercises

10.18 | If we assume that nitrogen uses sp^3 hybrid orbitals in NH_3, use valence bond theory to account for the formation of NH_4^+ from NH_3 and H^+. (*Hint:* Which atom donates the pair of electrons in the formation of the bond between H^+ and NH_3?)

10.19 | What is the shape of the PCl_6^- ion? What hybrid orbitals are used by phosphorus in PCl_6^-? Draw the orbital diagram for phosphorus in PCl_6^-.

10.6 | Hybrid Orbitals and Multiple Bonds

The types of orbital overlap that we have described so far produce bonds in which the electron density is concentrated most heavily between the nuclei of the two atoms along an imaginary line that joins their centers. Any bond of this kind, whether formed from the overlap of *s* orbitals, *p* orbitals, or hybrid orbitals (Figure 10.30), is called a **sigma bond** (or **σ bond**).

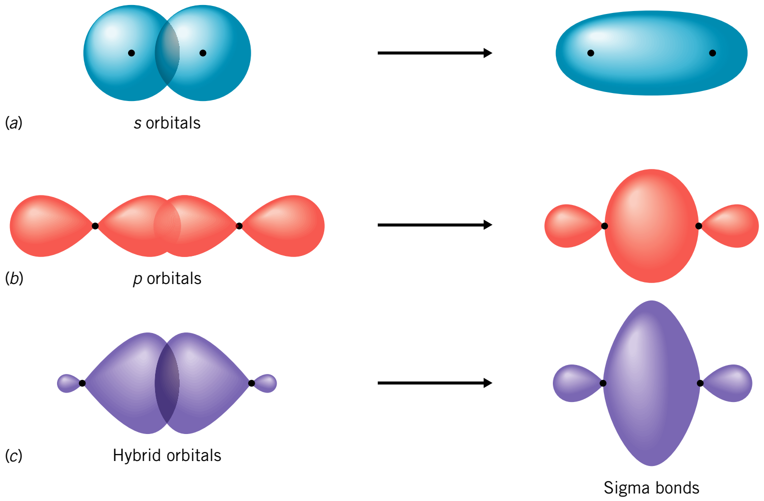

(a)
s orbitals
(b)
p orbitals
(c)
Hybrid orbitals
Sigma bonds

Figure 10.30 | **Formation of σ bonds.** Sigma bonds concentrate electron density along the line between the two atoms joined by the bond. (*a*) From the overlap of *s* orbitals. (*b*) From the end-to-end overlap of *p* orbitals. (*c*) From the overlap of hybrid orbitals.

Another way that *p* orbitals can overlap is shown in Figure 10.31. This produces a bond in which the electron density is divided between two separate regions that lie on opposite sides of an imaginary line joining the two nuclei. This kind of bond is called a **pi bond**

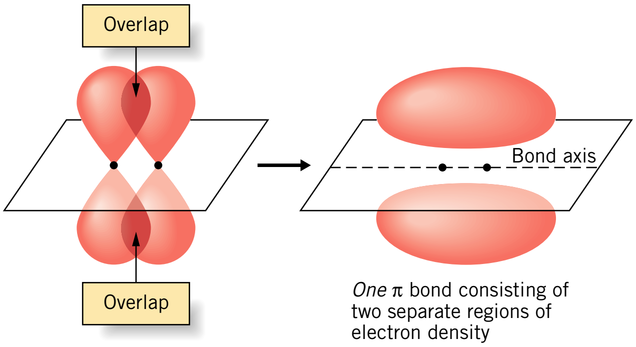
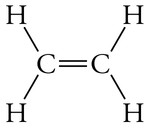

Overlap
Overlap
Bond axis
One π bond consisting of two separate regions of electron density

Figure 10.31 | **Formation of a π bond.** Two *p* orbitals overlap sideways instead of end-to-end. The electron density is concentrated in two regions on opposite sides of the bond axis, and taken together they constitute one π bond.

(or π **bond**). Notice that a π bond, like a *p* orbital, consists of two parts, and each part makes up just half of the π bond; it takes both of them to equal one π bond. The formation of π bonds allows atoms to form double and triple bonds.

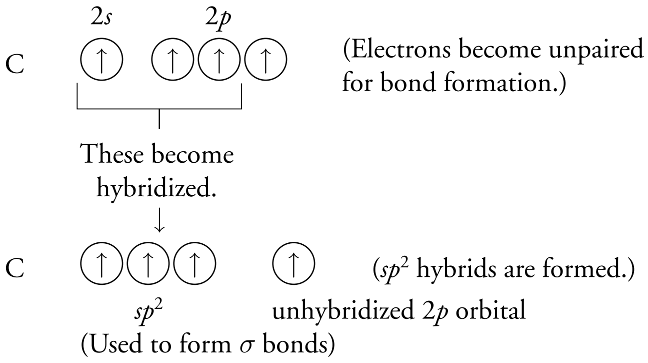
Double Bonds

A hydrocarbon that contains a double bond is ethene (also called ethylene), C_2H_4. It has the Lewis structure



ethene
(ethylene)

The molecule is planar, and each carbon atom lies in the center of a triangle surrounded by three other atoms (two H and one C atom). A planar triangular arrangement of bonds suggests that carbon uses sp^2 hybrid orbitals. Therefore, let's look at the distribution of electrons among the orbitals that carbon has available in its valence shell, assuming sp^2 hybridization.


2s
2p
C
(Electrons become unpaired
for bond formation.)
These become
hybridized.
C
(sp^2 hybrids are formed.)
sp^2
(Used to form σ bonds)
unhybridized 2*p* orbital

Notice that the carbon atom has an unpaired electron in an unhybridized 2*p* orbital. This *p* orbital is oriented perpendicular to the triangular plane of the sp^2 hybrid orbitals, as shown in Figure 10.32. Now we can see how the molecule goes together.

The basic framework of the molecule is determined by the formation of σ bonds. Each carbon uses two of its sp^2 hybrids to form σ bonds to hydrogen atoms. The third sp^2 hybrid on each carbon is used to form a σ bond between the two carbon atoms, thereby accounting for one of the two bonds of the double bond. Finally, the remaining unhybridized 2*p* orbitals, one from each carbon atom, overlap to produce a π bond, which accounts for the second bond of the double bond.

■ The double bond is a little like a hot dog on a bun. The sigma bond is like the hot dog, and the π bond is like the two parts of the bun.

This description of the bonding in C_2H_4 accounts for one of the most important properties of double bonds: rotation of one portion of the molecule relative to the rest around the axis of the double bond occurs only with great difficulty. The reason for this is illustrated in Figure 10.33. We see that as one CH_2 group rotates relative to the other around the carbon–carbon bond, the unhybridized *p* orbitals become misaligned and can no longer overlap effectively. This destroys the π bond. In effect, then, rotation around a double bond involves bond breaking, which requires more energy than is normally available to molecules at room temperature. As a result, rotation around the axis of a double bond usually doesn't take place.

■ Restricted rotation around double bonds affects the properties of organic and biochemical molecules.

In almost every instance, a double bond consists of a σ bond and a π bond. Another example is the compound methanal (better known as formaldehyde, the substance used as

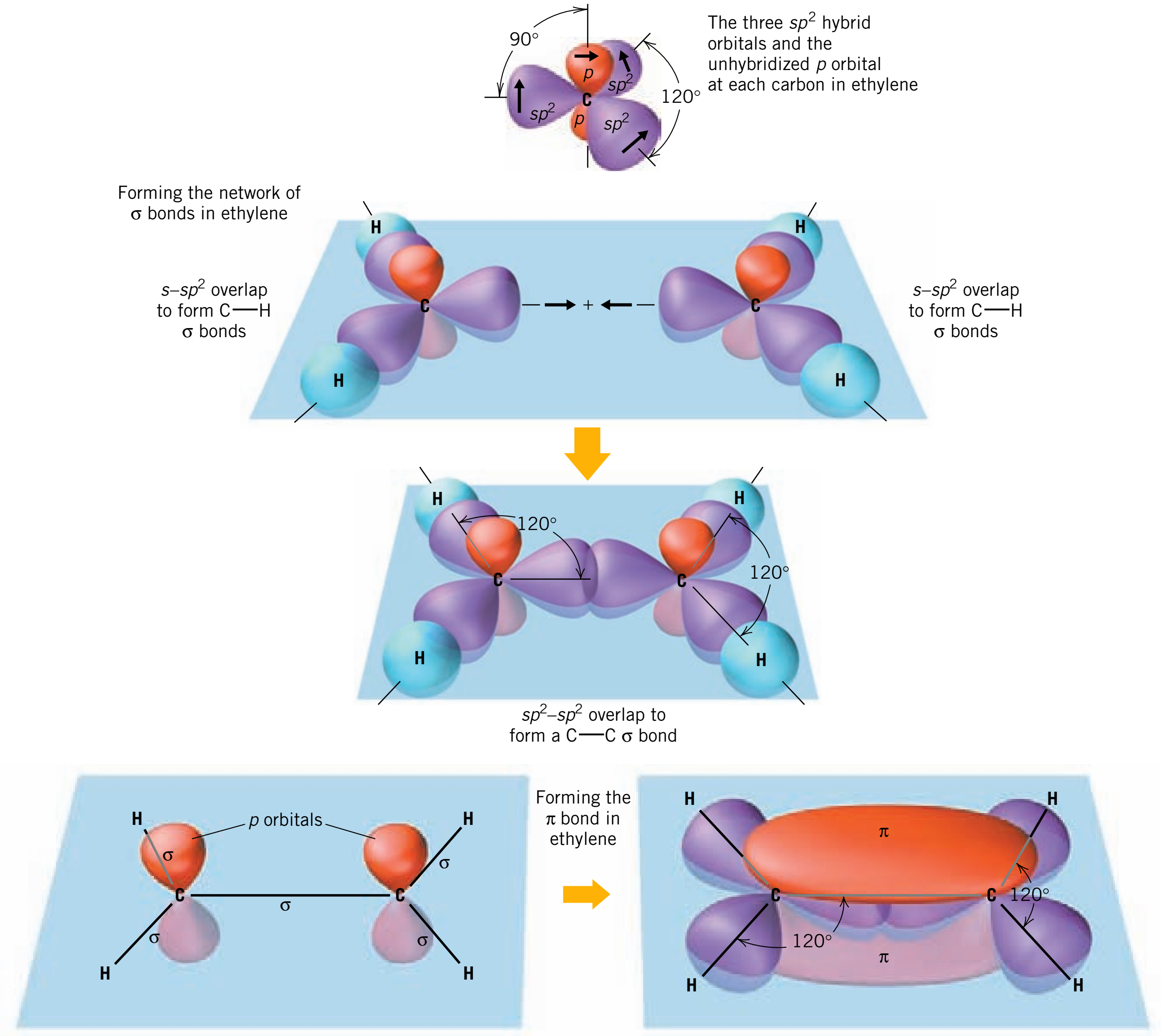

90°
p
sp2
C
sp2
p
sp2
120°
The three sp2 hybrid orbitals and the unhybridized p orbital at each carbon in ethylene
Forming the network of σ bonds in ethylene
s–sp2 overlap to form C—H σ bonds
H
C
+
C
H
s–sp2 overlap to form C—H σ bonds
H
H
120°
120°
H
C
C
H
H
H
sp2–sp2 overlap to form a C—C σ bond
H
p orbitals
H
σ
σ
C
σ
C
σ
σ
H
H
Forming the π bond in ethylene
H
H
π
C
C
120°
120°
π
H
H

Figure 10.32 | **The carbon–carbon double bond.**

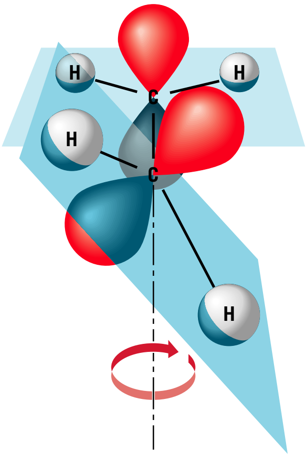
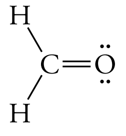


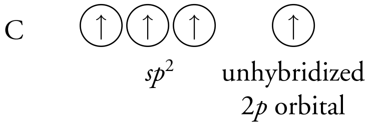
Figure 10.33 | **Restricted rotation around a double bond.** As the CH_2 group closest to us rotates relative to the one at the rear, the unhybridized *p* orbitals become misaligned, as shown here. This destroys the overlap and breaks the π bond. Bond breaking requires a lot of energy, more than is available to the molecule through the normal bending and stretching of its bonds at room temperature. Because of this, rotation around the double bond axis is hindered or "restricted."

a preservative for biological specimens and as an embalming fluid). The Lewis structure of this compound is

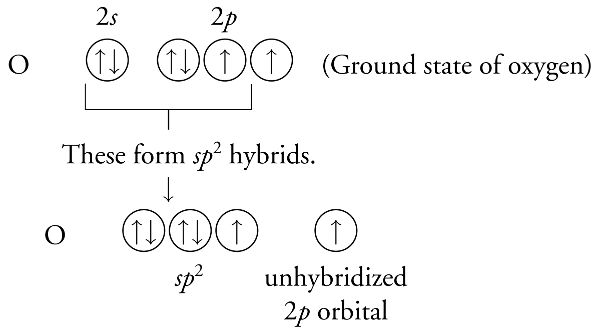


formaldehyde

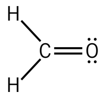
As with ethene, the carbon forms sp^2 hybrids, leaving an unpaired electron in an unhybridized p orbital.


C
sp^2
unhybridized
$2p$ orbital

The oxygen can also form sp^2 hybrids, with electron pairs in two of them and an unpaired electron in the third. This means that the remaining unhybridized p orbital also has an unpaired electron.

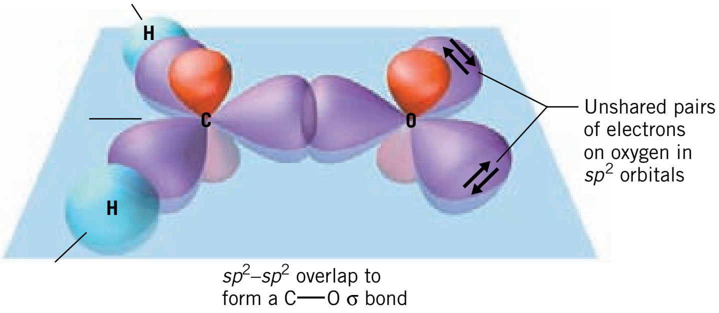

$2s$
$2p$
O
(Ground state of oxygen)
These form sp^2 hybrids.
O
sp^2
unhybridized
$2p$ orbital

■ The two filled sp^2 hybrids on the oxygen become lone pairs on the oxygen atom in the molecule.



Formaldehyde

Figure 10.34 shows how the carbon, hydrogen, and oxygen atoms form the molecule. As before, the basic framework of the molecule is formed by the σ bonds. These determine


H
C
O
H
Unshared pairs of electrons on oxygen in sp^2 orbitals
sp^2–sp^2 overlap to form a C—O σ bond

Forming the π bond in formaldehyde

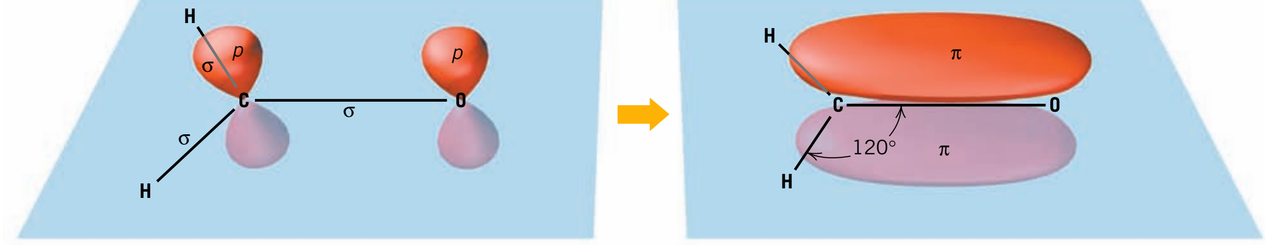

H
σ
p
C
σ
p
O
σ
H
H
π
C
O
120°
π
H

Figure 10.34 | **Bonding in formaldehyde.** The carbon–oxygen double bond consists of a σ bond and a π bond. The σ bond is formed by the overlap of sp^2 hybrid orbitals. The overlap of unhybridized p orbitals on the two atoms gives the π bond.

the molecular shape. The carbon–oxygen double bond also contains a π bond formed by the overlap of the unhybridized *p* orbitals.

Triple Bonds

An example of a molecule containing a triple bond is ethyne, also known as acetylene, C_2H_2 (a gas used as a fuel for welding torches).

$$\mathrm{H{-}C{\equiv}C{-}H}$$

ethyne
(acetylene)

In the linear ethyne molecule, each carbon needs two hybrid orbitals to form two σ bonds—one to a hydrogen atom and one to the other carbon atom. These can be provided by mixing the 2*s* and one of the 2*p* orbitals to form *sp* hybrids. To help us visualize the bonding, we will imagine that there is an *xyz* coordinate system centered at each carbon atom and that it is the $2p_z$ orbital that becomes mixed in the hybrid orbitals.

■ We label the orbitals p_x, p_y, and p_z just for convenience; they are really all equivalent.

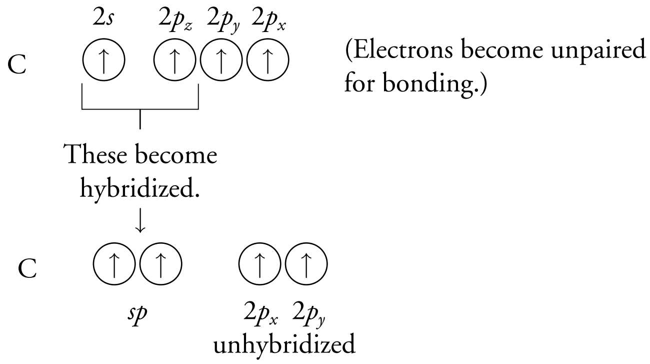


Figure 10.35 shows how the bonds in the molecule are formed. The *sp* orbitals point in opposite directions and are used to form the σ bonds. The unhybridized $2p_x$ and $2p_y$ orbitals are perpendicular to the C—C bond axis and overlap sideways to form two separate π bonds that surround the C—C σ bond. Notice that we now have three pairs of electrons in three bonds—one σ bond and two π bonds—whose electron densities are concentrated in different places. Also notice that the use of *sp* hybrid orbitals for the σ bonds allows us to explain the linear arrangement of atoms in the molecule.

Similar descriptions can be used to explain the bonding in other molecules that have triple bonds. Figure 10.36, for example, shows how the nitrogen molecule, N_2, is formed. In it, too, the triple bond is composed of one σ bond and two π bonds.

Sigma Bonds and Molecular Structure

In the preceding discussions we examined several polyatomic molecules that contain both single and multiple bonds. The following observations will be helpful in applying the valence bond theory to a variety of similar molecules.

A Brief Summary

1. The basic molecular framework of a molecule is determined by the arrangement of its σ bonds.
2. Hybrid orbitals are used by an atom to form its σ bonds and to hold lone pairs of electrons.
3. The number of hybrid orbitals needed by an atom in a structure equals the number of atoms to which it is bonded *plus* the number of lone pairs of electrons in its valence shell.
4. When there is a double bond in a molecule, it consists of one σ bond and one π bond.
5. When there is a triple bond in a molecule, it consists of one σ bond and two π bonds.

TOOLS

σ and π bonds and hybridization

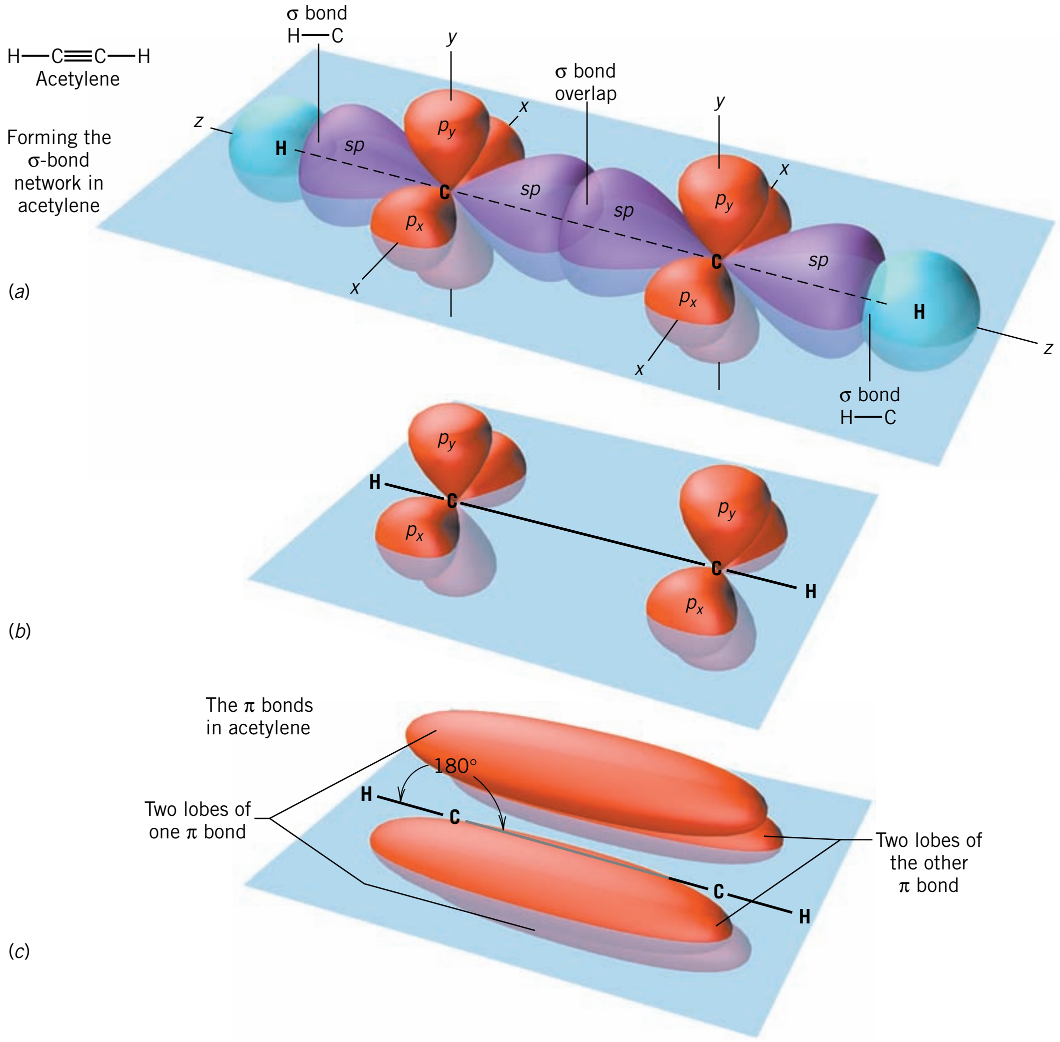
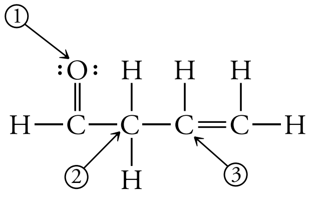

σ bond
H—C
H—C≡C—H
Acetylene
Forming the σ-bond network in acetylene
y
σ bond overlap
y
z
x
x
H
sp
p_y
sp
sp
p_y
C
p_x
C
sp
p_x
x
x
H
z
σ bond
H—C
(a)
p_y
H
C
p_y
p_x
C
H
p_x
(b)
The π bonds in acetylene
180°
H
C
Two lobes of one π bond
Two lobes of the other π bond
C
H
(c)

Figure 10.35 | **The carbon–carbon triple bond in ethyne.** (*a*) The *sp* hybrid orbitals on the carbon atoms are used to form sigma bonds to the hydrogen atoms and to each other. This accounts for one of the three bonds between the carbon atoms. (*b*) Sideways overlap of unhybridized $2p_x$ and $2p_y$ orbitals of the carbon atoms produces two π bonds. (*c*) The two π bonds in acetylene after they've formed surround the σ bond.

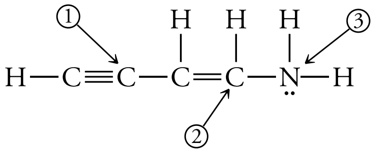
Practice Exercises

10.20 | Consider the molecule below. What kind of hybrid orbitals are used by atoms 1, 2, and 3? How many sigma bonds and pi bonds are in the molecule? (*Hint:* Study the brief summary above.)



$\mathrm{H{-}C({=}\ddot{O}{:}){-}CH_2{-}CH{=}CH{-}H}$

10.21 | Consider the molecule below. What kind of hybrid orbitals are used by atoms 1, 2, and 3? How many σ bonds and π bonds are in the molecule?



$\mathrm{H{-}C{\equiv}C{-}CH{=}CH{-}\ddot{N}H{-}H}$

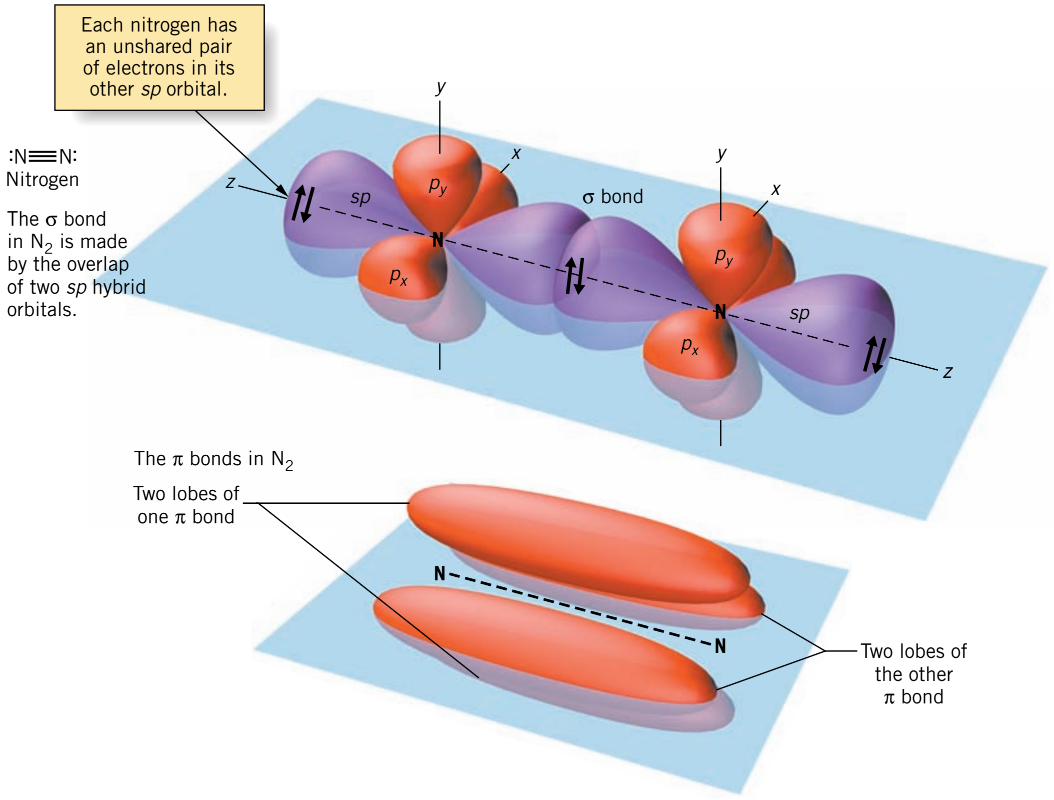

Each nitrogen has an unshared pair of electrons in its other *sp* orbital.
$:N{\equiv}N:$
Nitrogen
The σ bond in N_2 is made by the overlap of two *sp* hybrid orbitals.
y
x
z
sp
p_y
p_x
N
σ bond
y
x
p_y
N
sp
p_x
z
The π bonds in N_2
Two lobes of one π bond
N
N
Two lobes of the other π bond

Figure 10.36 | **Bonding in molecular nitrogen.** The triple bond in nitrogen, N_2, is formed like the triple bond in ethyne. A sigma bond is formed by the overlap of *sp* hybrid orbitals. The two unhybridized 2*p* orbitals on each nitrogen atom overlap to give the two π bonds. On each nitrogen, there is a lone pair of electrons in the *sp* hybrid orbital that's not used to form the sigma bond.

10.7 | Molecular Orbital Theory Basics

Molecular orbital theory takes the view that molecules and atoms are alike in one important respect. Both have energy levels that correspond to various orbitals that can be populated by electrons. In atoms, these orbitals are called atomic orbitals; in molecules, they are called **molecular orbitals.** (We shall frequently call them MOs.)

In most cases, the actual shapes and energies of molecular orbitals cannot be determined exactly. Nevertheless, reasonably good estimates of their shapes and energies can be obtained by combining the electron waves corresponding to the atomic orbitals of the atoms that make up the molecule. In forming molecular orbitals, these waves interact by constructive and destructive interference just like other waves we've seen. Their intensities are either added or subtracted when the atomic orbitals overlap.

Formation of Molecular Orbitals from Atomic Orbitals

In Chapter 8 you learned that an atomic orbital is represented mathematically by a wave function, ψ, and that the square of the wave function, ψ^2, describes the distribution of electron density around the nucleus. In MO theory, molecular orbitals are also represented by wave functions, ψ_{MO}, that when squared describe the distribution of electron density around the entire set of nuclei that make up the molecule.

■ When the wave function is squared, it allows us to calculate the probability of finding the electron at different points in an atom or molecule. By squaring the wave function, a positive probability is obtained regardless of the algebraic sign of the original function.

■ The number of MOs formed is always equal to the number of atomic orbitals that are combined.

One of the properties of wave functions in general is they can have positive or negative algebraic signs in different regions of space. Let's look at two examples: the wave functions for a 1*s* orbital and for a 2*p* orbital. The 1*s* orbital has a positive sign in all regions, and we can indicate this as shown in Figure 10.37. The wave function for a 2*p* orbital, on the other hand, has a positive sign for one of its two lobes and a negative sign for the other (Figure 10.37). The signs of the wave functions become important when the orbitals combine to form molecular orbitals.

Theoreticians have found that they can obtain reasonable estimates of MO wave functions by mathematically adding and subtracting the wave functions for a pair of overlapping atomic orbitals. Adding the atomic orbitals gives one ψ_{MO}, and subtracting them gives another ψ_{MO}. This gives *two* molecular orbitals with special properties, as illustrated in Figure 10.38 for two overlapping 1*s* orbitals centered on different nuclei. (For subtraction, the sign of one of the orbitals is changed before being added to the other, which is equivalent to subtracting one from the other.) The vertical scale in Figure 10.38 is energy and illustrates that when the atomic orbitals are combined by addition, the resulting MO has a lower energy than the two 1*s* atomic orbitals. This is because by adding the atomic orbitals, ψ_{MO} (and ψ^2_{MO}) becomes large in regions between the nuclei where the atomic orbitals overlap. Stated another way, adding atomic orbitals produces a molecular orbital that concentrates electron density between the nuclei and leads to a lowering of the energy. This type of molecular orbital helps to stabilize a molecule when occupied by electrons and is called a **bonding molecular orbital.**

In Figure 10.38 we also see what happens when one 1*s* orbital is subtracted from the other 1*s* orbital. This also yields a molecular orbital, but the magnitude of ψ_{MO} becomes smaller between the nuclei where the atomic orbitals overlap. In fact, halfway between the nuclei the atomic orbital wave functions have the same magnitude but opposite sign, so when they are combined the resulting ψ_{MO} has a value of zero. As a result, between the two nuclei there is a nodal plane on which ψ_{MO} is equal to zero. On this plane ψ^2_{MO} is zero and the electron density drops to zero. Notice that this MO, which is called an **antibonding molecular orbital,** has a higher energy than either of the two 1*s* atomic orbitals. This is because the electron density is reduced between the nuclei, causing the internuclear repulsions to outweigh their attractions for the electron density that remains between the nuclei. Antibonding molecular orbitals tend to destabilize a molecule when occupied by electrons.

Another thing to notice in Figure 10.38 is that both MOs have their maximum electron density on an imaginary line that passes through the two nuclei, giving them properties of sigma bonds. MOs like this are also designated as sigma (σ), with a subscript showing which atomic orbitals make up the MO and an asterisk indicating which is anti-

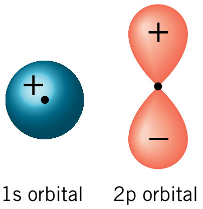


Figure 10.37 | **Algebraic signs of the wave functions for 1*s* and 2*p* atomic orbitals.** The wave function for a 1*s* orbital is positive everywhere. The wave funcion for a 2*p* orbital is positive for one lobe and negative for the other.

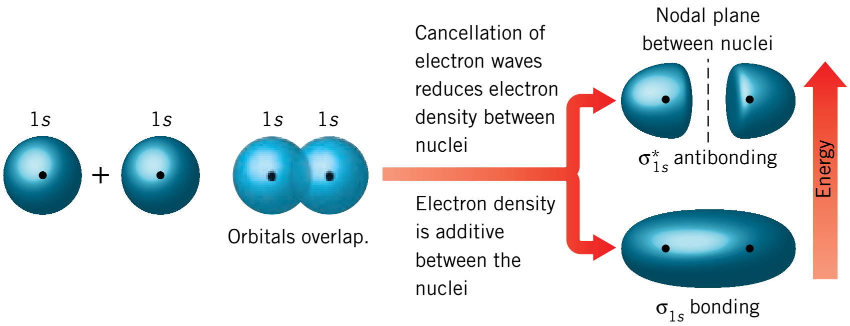

1s
+
1s
1s
1s
Orbitals overlap.
Cancellation of electron waves reduces electron density between nuclei
Nodal plane between nuclei
σ*1s antibonding
Electron density is additive between the nuclei
σ1s bonding
Energy

Figure 10.38 | **Combining 1*s* atomic orbitals to produce bonding and antibonding molecular orbitals.** These are σ-type orbitals because the electron density is concentrated along the imaginary line that passes through both nuclei. The antibonding orbital has a nodal plane between the nuclei where ψ_{MO}, ψ^2_{MO}, and the electron density drop to zero.

bonding. Thus, the bonding and antibonding MOs formed by overlap of 1*s* orbitals are symbolized as σ_{1s} and σ^*_{1s}, respectively.

It is always true that bonding MOs are lower in energy than antibonding MOs formed from the same atomic orbitals, as shown in Figure 10.38. When electrons populate molecular orbitals, they fill the lower energy, bonding MOs first. The rules that apply to filling MOs are the same as those for filling atomic orbitals: *Electrons spread out over molecular orbitals of equal energy (Hund's rule) and two electrons can only occupy the same orbital if their spins are paired.* When filling the MOs, we also have to be sure we've accounted for all of the valence electrons of the separate atoms.

Why H_2 Exists but He_2 Does Not

Figure 10.39*a* is an MO energy level diagram for H_2. The energies of the separate 1*s* atomic orbitals are indicated at the left and right; those of the molecular orbitals are shown in the center. The H_2 molecule has two electrons, and both can be placed in the σ_{1s} orbital. The shape of this bonding orbital, shown in Figure 10.38, should be familiar. It's the same as the shape of the electron cloud that we described using the valence bond theory.

Next, let's consider what happens when two helium atoms come together. Why can't a stable molecule of He_2 be formed? Figure 10.39*b* is the energy diagram for He_2. Notice that both bonding and antibonding orbitals are filled. In situations such as this there is a net destabilization because the antibonding MO is raised in energy more than the bonding MO is lowered, relative to the orbitals of the separated atoms. This means the total energy of He_2 is larger than that of two separate He atoms, so the "molecule" is unstable and immediately comes apart.

In general, the effects of **antibonding electrons** (those in antibonding MOs) cancel the effects of an equal number of **bonding electrons**, and molecules with equal numbers of bonding and antibonding electrons are unstable. If we remove an antibonding electron from He_2 to give He_2^+, there is a net excess of bonding electrons, and the ion should be capable of existence. In fact, the emission spectrum of He_2^+ can be observed when an electric discharge is passed through a helium-filled tube, which shows that He_2^+ is present during the electric discharge. However, the ion is not very stable and cannot be isolated.

Bond Order

The concept of bond order was introduced in Section 9.8 where it was defined as the number of pairs of electrons shared between two atoms. To translate the MO description into these terms, we compute the bond order as follows:

$$\text{Bond order} = \frac{(\text{number of bonding } e^-) - (\text{number of antibonding } e^-)}{2 \text{ electrons/bond}}$$

TOOLS

MO bond order

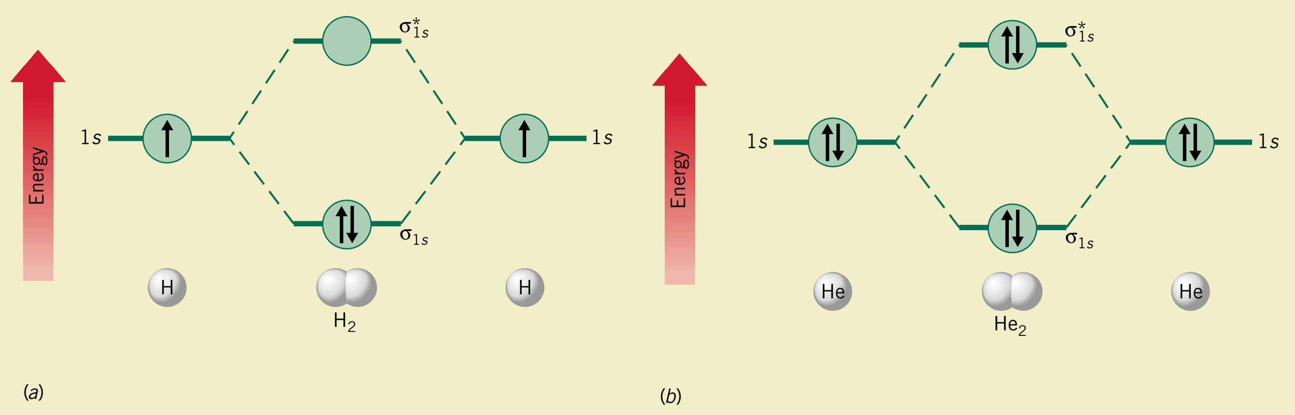


Figure 10.39 | **Molecular orbital descriptions of H_2 and He_2.** (*a*) Molecular orbital energy-level diagram for H_2. (*b*) Molecular orbital energy-level diagram for He_2.

For the H_2 molecule, we have

$$\text{Bond order} = \frac{2-0}{2} = 1$$

A bond order of 1 corresponds to a single bond. For He_2 we have

$$\text{Bond order} = \frac{2-2}{2} = 0$$

A bond order of zero means there is no bond, so the He_2 molecule is unable to exist. For the $He_2{}^+$ ion, which *is* able to form, the calculated bond order is

$$\text{Bond order} = \frac{2-1}{2} = 0.5$$

Notice that the bond order does not have to be a whole number. In this case, it indicates a bond character equivalent to about half a bond.

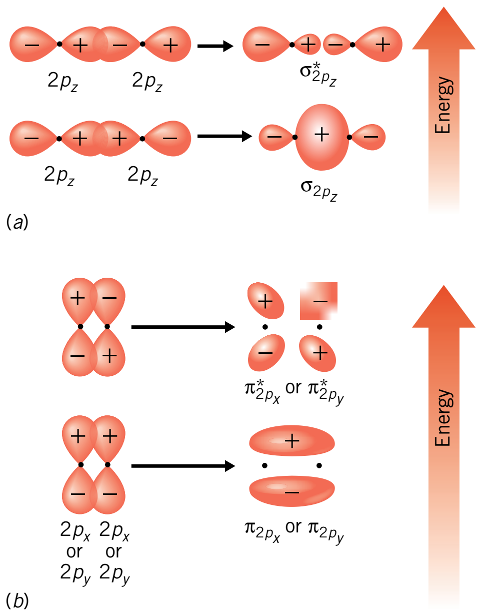


Figure 10.40 | **Formation of molecular orbitals by the overlap of *p* orbitals.** Where overlapping parts of the 2*p* orbitals have the same algebraic sign, a bonding MO is formed; where the signs are opposite, an antibonding MO is formed. (*a*) Two $2p_z$ orbitals that point at each other combine to give bonding and antibonding σ-type MOs. (*b*) Perpendicular to the $2p_z$ orbitals are $2p_x$ and $2p_y$ orbitals that overlap to give two sets of bonding and antibonding π-type MOs.

MO Description of Homonuclear Diatomic Molecules of Period 2

A **homonuclear diatomic molecule** is one in which both atoms are of the same element. Examples are N_2 and O_2, in which both elements are found in Period 2. As you have learned, the outer shell of a Period 2 element consists of 2*s* and 2*p* subshells. When atoms of this period bond to each other, the atomic orbitals of these subshells interact strongly to produce molecular orbitals. The 2*s* orbitals, for example, overlap to form σ_{2s} and σ^*_{2s} molecular orbitals having essentially the same shapes as the σ_{1s} and σ^*_{1s} MOs, respectively. Figure 10.40 shows the shapes of the bonding and antibonding MOs produced when the 2*p* orbitals overlap. If we label those that point toward each other as $2p_z$, a set of bonding and antibonding MOs are formed that we can label as σ_{2p_z} and $\sigma^*_{2p_z}$. The $2p_x$ and $2p_y$ orbitals, which are perpendicular to the $2p_z$ orbitals, overlap sideways to give π-type molecular orbitals. They are labeled π_{2p_x} and $\pi^*_{2p_x}$, and π_{2p_y} and $\pi^*_{2p_y}$, respectively. Notice in Figure 10.40 that we have indicated the algebraic signs of the 2*p* orbital wave functions. When the 2*p* orbitals overlap with the same sign, bonding MOs are formed, and when the signs are reversed, antibonding MOs are formed. In the bonding MOs, electron density is increased in the region between the two nuclei, whereas in antibonding MOs, electron density is reduced between the nuclei.

The approximate relative energies of the MOs formed from the second shell atomic orbitals are shown in Figure 10.41. Notice that from Li to N, the energies of the π_{2p_x} and π_{2p_y} orbitals are lower than the energy of the σ_{2p_z}. Then from O to Ne, the energies of the two levels are reversed. The reasons for this are complex and beyond the scope of this book.

Using Figure 10.41, we can predict the electronic structures of diatomic molecules of Period 2. These *MO electron configurations* are obtained using the same rules that are applied to the filling of atomic orbitals in atoms, as noted earlier.

TOOLS

How electrons fill MOs

How Electrons Fill Molecular Orbitals

1. Electrons fill the lowest energy orbitals that are available.
2. No more than two electrons, with spins paired, can occupy any orbital.
3. Electrons spread out as much as possible, with spins unpaired, over orbitals that have the same energy.

Applying these rules to the valence electrons of Period 2 atoms gives the MO electron configurations shown in Table 10.1. Let's see how well MO theory performs by examining data that are available for these molecules.

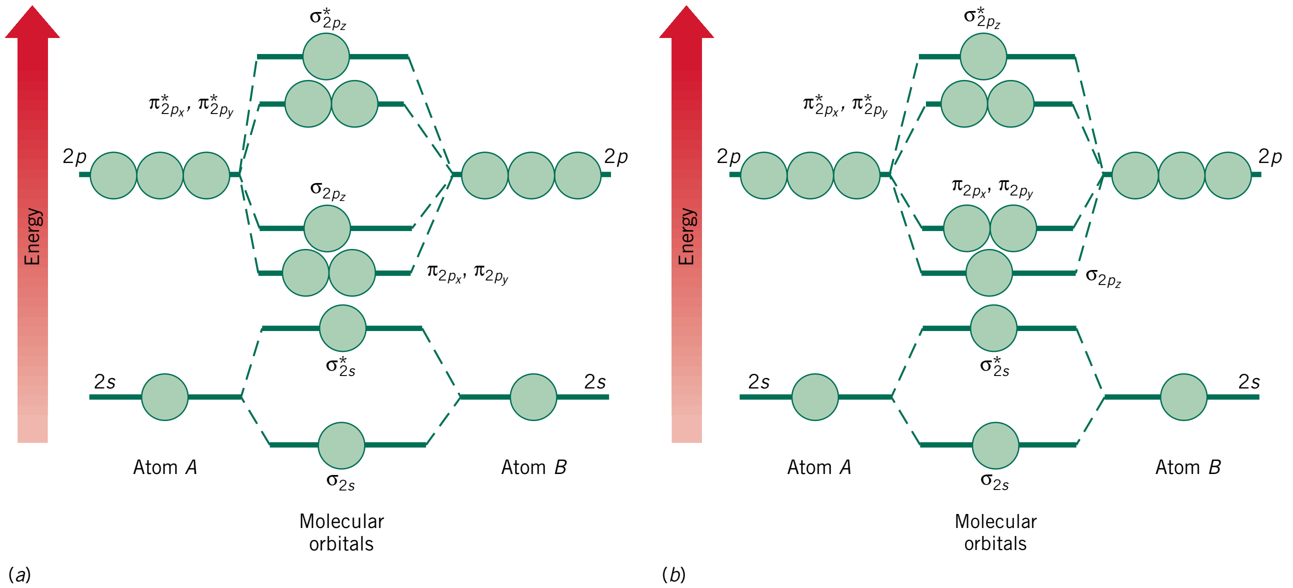

Energy
$\sigma^*_{2p_z}$
$\pi^*_{2p_x}$, $\pi^*_{2p_y}$
2p
2p
σ_{2p_z}
π_{2p_x}, π_{2p_y}
σ^*_{2s}
2s
2s
σ_{2s}
Atom A
Atom B
Molecular orbitals
(a)
Energy
$\sigma^*_{2p_z}$
$\pi^*_{2p_x}$, $\pi^*_{2p_y}$
2p
2p
π_{2p_x}, π_{2p_y}
σ_{2p_z}
σ^*_{2s}
2s
2s
σ_{2s}
Atom A
Atom B
Molecular orbitals
(b)

Figure 10.41 | **Approximate relative energies of molecular orbitals in Period 2 diatomic molecules.** *(a)* Li_2 through N_2. *(b)* O_2 through Ne_2.

According to Table 10.1, MO theory predicts that molecules of Be_2 and Ne_2 should not exist at all because they have bond orders of zero. In beryllium vapor and in gaseous neon, no evidence of Be_2 or Ne_2 has ever been found. MO theory also predicts that diatomic molecules of the other Period 2 elements should exist because they all have bond orders greater than zero. These molecules have, in fact, been observed. Although lithium, boron, and carbon are complex solids under ordinary conditions, they can be vaporized. In the vapor, molecules of Li_2, B_2, and C_2 can be detected. Nitrogen, oxygen, and fluorine, as you know, are gaseous elements that exist as N_2, O_2, and F_2.

Table 10.1 Molecular Orbital Populations and Bond Orders for Period 2 Diatomic Molecules[a]

		Li_2	Be_2	B_2	C_2	N_2			O_2	F_2	Ne_2
Energy ↑	$\sigma^*_{2p_z}$	○	○	○	○	○	Energy ↑	$\sigma^*_{2p_z}$	○	○	(↑↓)
	$\pi^*_{2p_x}, \pi^*_{2p_y}$	○○	○○	○○	○○	○○		$\pi^*_{2p_x}, \pi^*_{2p_y}$	(↑)(↑)	(↑↓)(↑↓)	(↑↓)(↑↓)
	σ_{2p_z}	○	○	○	○	(↑↓)		π_{2p_x}, π_{2p_y}	(↑↓)(↑↓)	(↑↓)(↑↓)	(↑↓)(↑↓)
	π_{2p_x}, π_{2p_y}	○○	○○	(↑)(↑)	(↑↓)(↑↓)	(↑↓)(↑↓)		σ_{2p_z}	(↑↓)	(↑↓)	(↑↓)
	σ^*_{2s}	○	(↑↓)	(↑↓)	(↑↓)	(↑↓)		σ^*_{2s}	(↑↓)	(↑↓)	(↑↓)
	σ_{2s}	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)		σ_{2s}	(↑↓)	(↑↓)	(↑↓)
Number of Bonding Electrons		2	2	4	6	8			8	8	8
Number of Antibonding Electrons		0	2	2	2	2			4	6	8
Bond Order		1	0	1	2	3			2	1	0
Bond Energy (kJ/mol)		110	—	300	612	953			501	129	—
Bond Length (pm)		267	—	158	124	109			121	144	—

---

[a] Although the order of the energy levels corresponding to the σ_{2p_z}, and the π bonding MOs become reversed at oxygen, either sequence would yield the same result—a triple bond for N_2, a double bond for O_2, and a single bond for F_2.

In Table 10.1, we also see that the predicted bond order increases from boron to carbon to nitrogen and then decreases from nitrogen to oxygen to fluorine. As the bond order increases, the *net* number of bonding electrons increases, so the bonds should become stronger and the bond lengths shorter. The *experimentally measured* bond energies and bond lengths given in Table 10.1 agree with these predictions quite nicely.

Molecular orbital theory is particularly successful in explaining the electronic structure of the oxygen molecule. Experiments show that O_2 is paramagnetic (it's weakly attracted to a magnet) and that the molecule contains two unpaired electrons. In addition, the bond length in O_2 is about what is expected for an oxygen–oxygen double bond. These data cannot be explained by valence bond theory. For example, if we write a Lewis structure for O_2 that shows a double bond and also obeys the octet rule, all the electrons appear in pairs.

:Ö::Ö: (not acceptable based on experimental evidence because all electrons are paired)

■ Although MO theory easily handles the bonding situations that VB theory has trouble with, MO theory loses the simplicity of VB theory. For even quite simple molecules, MO theory is too complicated to make predictions without extensive calculations.

On the other hand, if we show the unpaired electrons, the structure has only a single bond and doesn't obey the octet rule.

:Ö:Ö: (not acceptable based on experimental evidence because of the O—O single bond)

With MO theory, we don't have any of these difficulties. By applying Hund's rule, the two electrons in the π^* orbitals of O_2 spread out over these orbitals with their spins unpaired because both orbitals have the same energy (see Table 10.1). The electrons in the two antibonding π^* orbitals cancel the effects of two electrons in the two bonding π orbitals, so the net bond order is 2 and the bond is effectively a double bond.

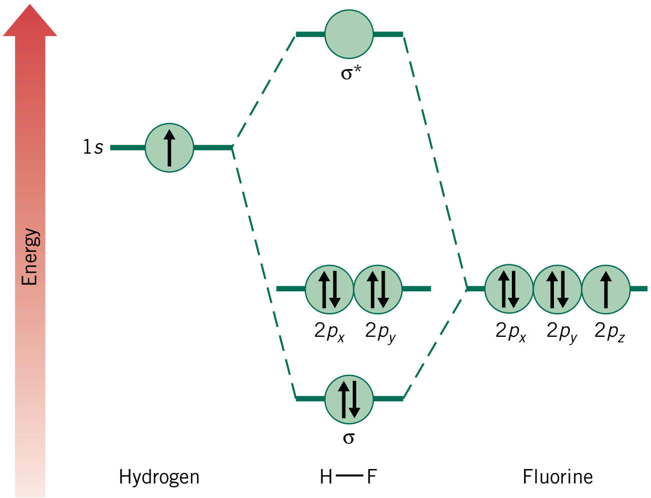


Figure 10.42 | **Molecular orbital energy diagram for HF.** Only the $1s$ orbital of hydrogen and the $2p$ orbitals of fluorine are shown.

Some Simple Heteronuclear Diatomic Molecules

As molecules become more complex, the simple application of MO theory becomes much more difficult. This is because it is necessary to consider the relative energies of the individual atomic orbitals as well as the orientations of the orbitals relative to those on other atoms. Nevertheless, we can take a brief look at the MO descriptions of a couple of diatomic molecules to see what happens when both atoms in the molecule are not the same. Such molecules are said to be **heteronuclear**.

Hydrogen Fluoride

When we consider the possible interaction of the orbitals of different atoms to form molecular orbitals, the first factor we have to consider is the relative energies of the orbitals. This is because orbitals interact most effectively when they are of about equal energy; the greater the difference in energy between the orbitals, the less the orbitals interact, and the more the orbitals behave like simple atomic orbitals.

In HF, the $1s$ orbital of hydrogen is higher in energy than either the $2s$ or $2p$ subshell of fluorine, but it is closest in energy to the $2p$ subshell (Figure 10.42). Taking the z axis as the internuclear axis, the hydrogen $1s$ orbital overlaps with the $2p_z$ orbital of fluorine to give bonding and antibonding σ-type orbitals, as illustrated in Figure 10.43. The $2p_x$ and $2p_y$ orbitals of fluorine, however, have no orbitals on hydrogen with which to interact, so they are unchanged when the molecule is formed. These two orbitals are said to be **nonbonding orbitals** because they are neither bonding nor antibonding; they have no effect on the stability of the molecule.

■ The $2s$ orbital of fluorine is so much lower in energy than the $2p$ subshell that we don't need to consider its interaction with the hydrogen $1s$ orbital. That's why it isn't shown in the energy diagram.

In the MO description of HF, we have a pair of electrons in the bonding MO formed by the overlap of the hydrogen $1s$ orbital with the fluorine $2p_z$ orbital. Earlier we saw that

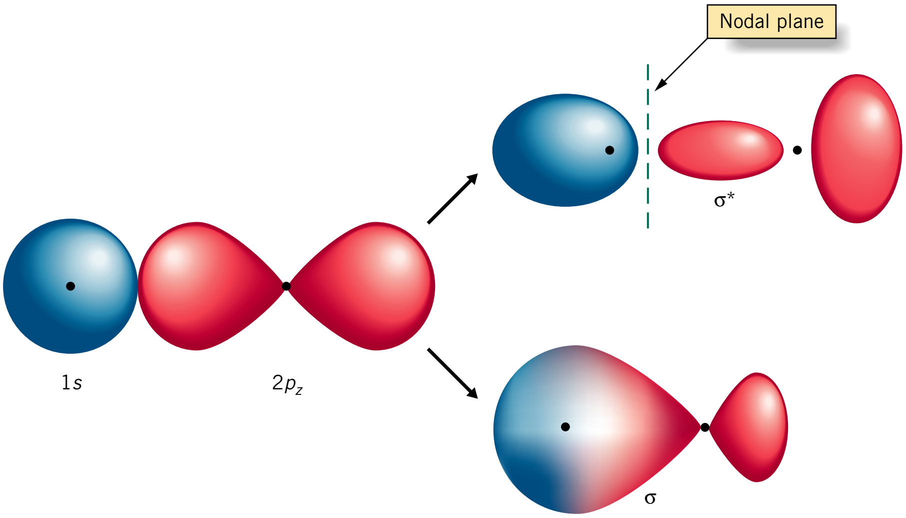


Figure 10.43 | **Formation of σ and σ^* orbitals in HF.** Once again, where overlapping atomic orbitals have the same sign, a bonding MO is formed; where the signs are opposite, an antibonding MO is formed. Notice that the antibonding σ^* orbital has a nodal plane between the nuclei, which effectively removes electron density from the region between the nuclei and, if occupied, leads to destabilization of the molecule.

valence bond theory explains the bond in HF in the same way—as a pair of electrons shared between the hydrogen 1*s* orbital and a fluorine 2*p* orbital.

Carbon Monoxide

Carbon monoxide is a heteronuclear molecule in which both atoms are from Period 2, so we expect the orbitals of the second shell to be the ones used to form the MOs. The orbital overlaps are similar to those of the homonuclear diatomics of Period 2, so the energy diagram resembles the one shown in Figure 10.41*a*.

Because the outer shell electrons of oxygen experience a larger effective nuclear charge than those of carbon, the oxygen orbitals will be somewhat lower in energy. This is shown in Figure 10.44. There are a total of 10 valence electrons (4 from carbon and 6 from

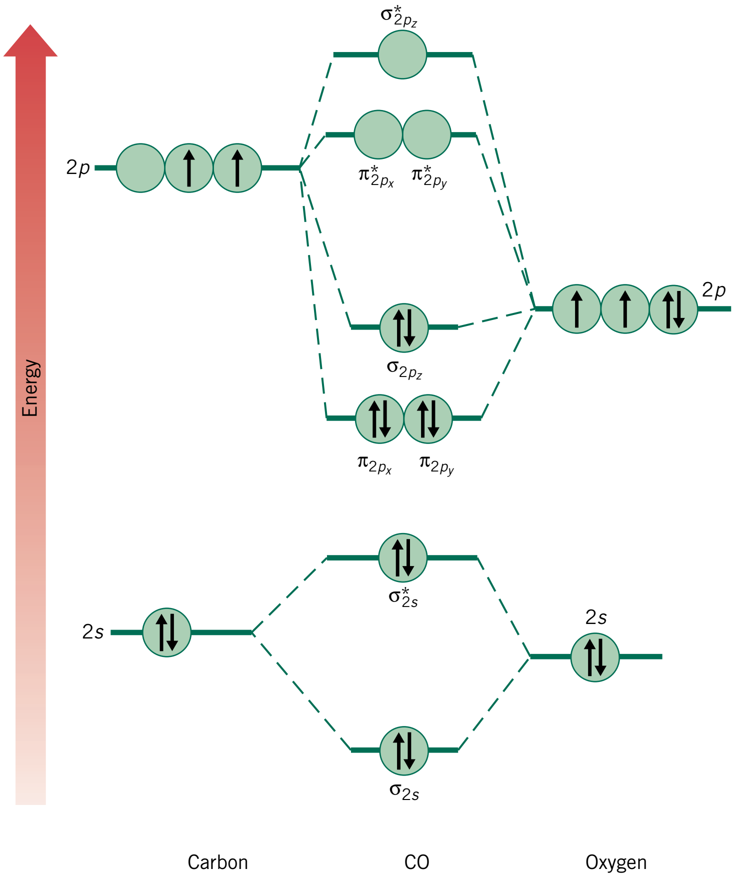


Figure 10.44 | **Molecular orbital energy diagram for carbon monoxide.** The oxygen orbitals are lower in energy than the corresponding carbon orbitals. The net bond order is 3.

oxygen) to distribute among the MOs of the molecule. When we do this, there are 8 bonding electrons and 2 antibonding electrons, so the net bond order is 3, corresponding to a triple bond. As expected, it consists of a σ bond and two π bonds.

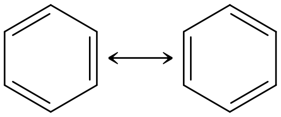
Practice Exercises

10.22 | The molecular orbital energy level diagram for the cyanide ion, CN^-, is similar to that of the earlier Period 2 homonuclear diatomics. Sketch the energy diagram for the ion and indicate the electron population of the MOs. What is the bond order in the ion? How does this agree with the bond order predicted from the Lewis structure of the ion? (*Hint:* How many valence electrons are there in the ion?)

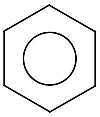
10.23 | The MO energy level diagram for the nitrogen monoxide molecule is essentially the same as that shown in Table 10.1 for O_2, except the oxygen orbitals are slightly lower in energy than the corresponding nitrogen orbitals. Sketch the energy diagram for nitrogen monoxide and indicate which MOs are populated. Calculate the bond order for the molecule. (*Hint:* Make adjustments to Figure 10.41*b*.)

10.8 | Delocalized Molecular Orbitals

One of the least satisfying aspects of the way valence bond theory explains chemical bonding is the need to write resonance structures for certain molecules and ions. For example, consider benzene, C_6H_6. As you learned earlier, this molecule has the shape of a ring whose resonance structures can be written as



The MO description of bonding in this molecule is as follows: The basic structure of the molecule is determined by the sigma-bond framework, which requires that the carbon atoms use sp^2 hybrid orbitals. This allows each carbon to form three σ bonds (two to other C atoms and one to an H atom) as illustrated in Figure 10.45*a*. Each carbon atom is left with a half-filled unhybridized *p* orbital perpendicular to the plane of the ring (Figure 10.45*b*). These *p* orbitals overlap to give a π-electron cloud that looks something like two doughnuts with the sigma-bond framework sandwiched between them (Figure 10.45*c*). The six electrons in this π-electron cloud spread over all six atoms in the ring and are said to be **delocalized** (i.e., they are not localized between any two atoms in the structure). The delocalized nature of the pi electrons is the reason we usually represent the structure of benzene as



One of the special characteristics of delocalized bonds is that they make a molecule or ion more stable than it would be if it had localized bonds. In Section 9.9 this was

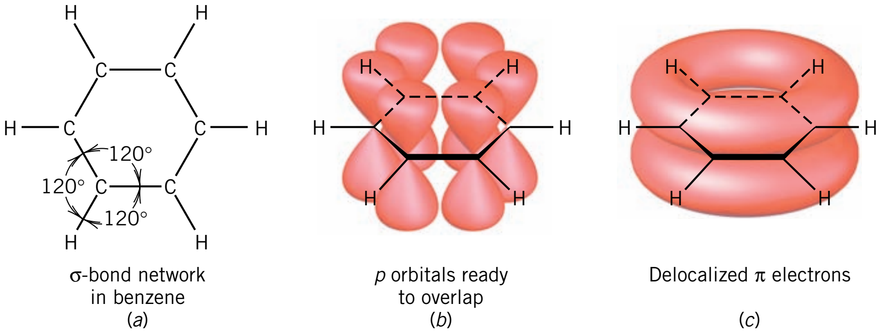


Figure 10.45 | **Benzene.**
(*a*) The σ-bond framework. All atoms lie in the same plane. (*b*) The unhybridized *p* orbitals at each carbon prior to side-to-side overlap. (*c*) The double doughnut-shaped electron cloud formed by the delocalized π electrons.

described in terms of *resonance energy*. In the molecular orbital theory, we no longer speak of resonance; instead, we refer to the electrons as being delocalized. The extra stability that is associated with this delocalization is therefore described, in the language of MO theory, as the **delocalization energy.**

■ Functionally, the terms ***resonance energy*** and ***delocalization energy*** are the same; they just come from different approaches to bonding theory.

10.9 | Bonding in Solids

Solids have some unique electrical properties that are familiar to everyone. For example, metals are good conductors of electricity, whereas nonmetallic substances are insulators; they are extremely poor electrical conductors. Between these extremes we find metalloids such as silicon and germanium, which are semiconductors; they are weak conductors of electricity. The theory developed to explain these widely differing properties is an extension of the principles of bonding discussed above and is called **band theory.**

According to band theory, an **energy band** in a solid is composed of a very large number of closely spaced energy levels that are formed by combining atomic orbitals of similar energy from each of the atoms within the substance. For example, in sodium the 1*s* atomic orbitals, one from each atom, combine to form a single 1*s* band. The number of energy levels in the band equals the number of 1*s* orbitals supplied by the entire collection of sodium atoms. The same thing occurs with the 2*s*, 2*p*, etc., orbitals, so that we also have 2*s*, 2*p*, etc., bands within the solid.

Figure 10.46 illustrates the energy bands in solid sodium. Notice that the electron density in the 1*s*, 2*s*, and 2*p* bands does not extend far from each individual nucleus, so these bands produce effectively localized energy levels in the solid. However, the 3*s* band (which is formed by overlap of the valence shell orbitals of the sodium atoms) is delocalized and extends continuously through the solid. The same applies to energy bands formed by higher-energy orbitals.

Sodium atoms have filled 1*s*, 2*s*, and 2*p* orbitals, so the corresponding bands in the solid are also filled. The 3*s* orbital of sodium, however, is only half-filled, which leads to a half-filled 3*s* band. The 3*p* and higher-energy bands in sodium are completely empty. When a voltage is applied across a piece of solid sodium, electrons in the half-filled 3s band can hop from atom to atom with ease, and this allows sodium to conduct electricity well. However, electrons in the lower-energy filled bands are unable to move through the solid because orbitals on neighboring atoms are already filled and cannot accept an additional electron. Such electrons do not contribute to the conductivity of the solid.

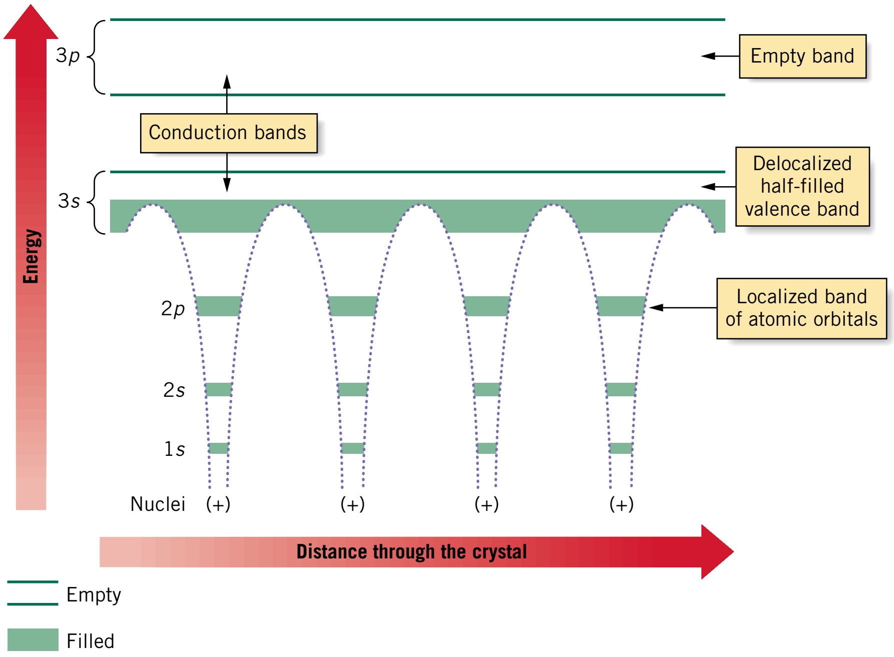

Energy
3p
Empty band
Conduction bands
3s
Delocalized half-filled valence band
2p
Localized band of atomic orbitals
2s
1s
Nuclei (+) (+) (+) (+)
Distance through the crystal
Empty
Filled

Figure 10.46 | **Energy bands in solid sodium.** The 1*s*, 2*s*, and 2*p* bands do not extend far in either direction from the nucleus, so the electrons in them are localized around each nucleus and can't move through the crystal. The delocalized 3*s* valence band extends throughout the entire solid, as do bands such as the 3*p* band formed from higher-energy orbitals of the sodium atoms.

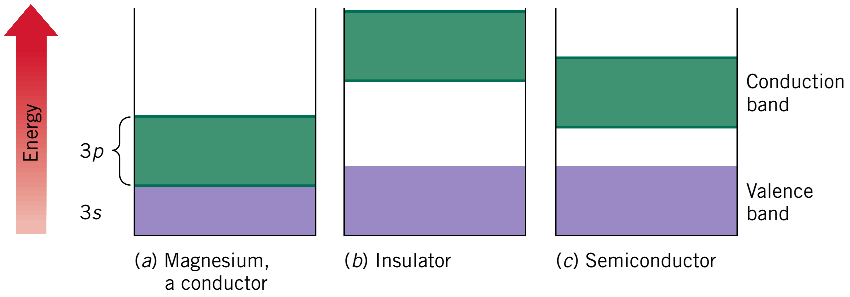


Figure 10.47 | **Energy bands in different types of solids.** (*a*) In magnesium, a good electrical conductor, the empty 3*p* conduction band overlaps the filled 3*s* valence band and provides a way for this metal to conduct electricity. (*b*) In an insulator, the energy gap between the filled valence band and the empty conduction band prevents electrons from populating the conduction band. (*c*) In a semiconductor, there is a small band gap, and thermal energy can promote some electrons from the filled valence band to the empty conduction band. This enables the solid to conduct electricity weakly.

We refer to the band containing the outer shell (valence shell) electrons as the **valence band.** Any band that is either vacant or partially filled and uninterrupted throughout the solid is called a **conduction band,** because electrons in it are able to move through the solid and thereby serve to carry electricity.

In metallic sodium the valence band and conduction band are the same, so sodium is a good conductor. In magnesium the 3*s* valence band is filled and therefore cannot be used to transport electrons. However, the vacant 3*p* conduction band actually overlaps the valence band and can easily be populated by electrons when voltage is applied (Figure 10.47*a*). This permits magnesium to be a conductor.

In an insulator such as glass, diamond, or rubber, all the valence electrons are used to form covalent bonds, so all the orbitals of the valence band are filled and cannot contribute to electrical conductivity. In addition, the energy separation, or **band gap,** between the filled valence band and the nearest conduction band (empty band) is large. As a result, electrons cannot populate the conduction band, so these substances are unable to conduct electricity (Figure 10.47*b*).

■ Recall that at any given temperature there is a distribution of kinetic energies among the particles of the substance. *Thermal energy* is kinetic energy a particle possesses because of its temperature. The higher the temperature, the higher the thermal energy.

In a semiconductor such as silicon or germanium, the valence band is also filled, but the band gap between the filled valence band and the nearest conduction band is small (Figure 10.47*c*). At room temperature, *thermal energy* (kinetic energy associated with the temperature of the substance) possessed by the electrons is sufficient to promote some electrons to the conduction band and a small degree of electrical conductivity is observed. One of the interesting properties of semiconductors is that their electrical conductivity increases with increasing temperature. This is because as the temperature rises, the number of electrons with enough energy to populate the conduction band also increases. Photons can also provide the energy needed to promote electrons to the conduction band. This happens, for example, with photoconductors such as cadmium sulfide.

Transistors and Other Electronic Devices

One of the most significant discoveries of the twentieth century was the way that the electrical characteristics of semiconductors can be modified by the controlled introduction of carefully selected impurities. This led to the discovery of transistors, which made possible all the marvelous electronic devices we now take for granted, such as iPods, digital cameras, cell phones, and personal computers. In fact, almost everything we do today is influenced in some way by electronic circuits etched into tiny silicon chips.

In a semiconductor such as silicon, all the valence electrons are used to form covalent bonds to other atoms. If a small amount of a Group 3A element such as boron is added to silicon, it can replace silicon atoms in the structure of the solid. (We say the silicon has been **doped** with boron.) However, for each boron added, one of the covalent bonds in the structure will be deficient in electrons because boron has only three valence electrons instead of the four that silicon has. Under an applied voltage, an electron from a neighboring atom can move to fill the deficiency and thereby leave a positive "hole" behind. This "hole" can then be filled by an electron from a neighboring atom, which creates a new "hole" on that atom. As this happens again and again, the positive "hole" migrates through the solid. The net result is an electrical conduction of a positive charge. Because of the positive nature of the moving charge carrier, the substance is said to be a **p-type semiconductor.**

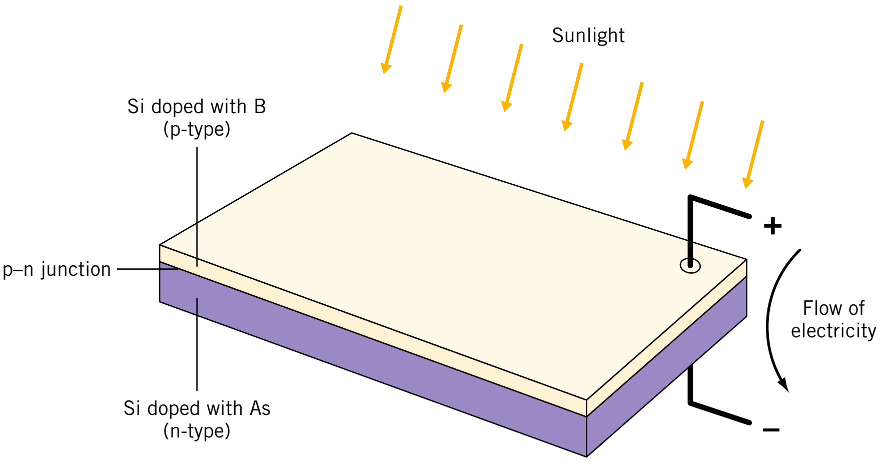


Figure 10.48 | **Construction of a silicon solar battery.**

If the impurity added to the silicon is a Group 5A element such as arsenic, it has one more electron in its valence shell than silicon. When the bonds are formed in the solid, there will be an electron left over that's not used in bonding. The extra electrons supplied by the impurity can enter the conduction band and move through the solid under an applied voltage, and because the moving charge now consists of electrons, which are negatively charged, the solid is said to be an **n-type semiconductor.**

Transistors are made from n- and p-type semiconductors and can be formed directly on the surface of a silicon chip, which has made possible the microcircuits in devices that seem to be everywhere around us.

Solar Cells

Another interesting application of semiconductors is in **solar cells** (also called **solar batteries**). These devices offer the potential of large scale harnessing of solar energy and are becoming more competitive with traditional forms of energy production as the price of solar cells drops.

A typical silicon solar cell is composed of a silicon wafer doped with arsenic (giving an n-type semiconductor) over which is placed a thin layer of silicon doped with boron (a p-type semiconductor). This is illustrated in Figure 10.48. In the dark there is an equilibrium between electrons and holes at the interface between the two layers, which is called a **p-n junction.** Some electrons from the n-type layer diffuse into the holes in the p-layer and are trapped. This leaves some positive holes in the n-layer. Equilibrium is achieved when the positive holes in the n-layer prevent further movement of electrons into the p-layer.

When light falls on the surface of the cell, the equilibrium is upset. Energy is absorbed, which permits electrons that were trapped in the p-layer to return to the n-layer. As these electrons move across the p-n junction into the n-layer, other electrons leave the n-layer through the wire, pass through the electrical circuit, and enter the p-layer. Thus an electric current flows when light falls on the cell and the external circuit is completed. This electric current can be used to run a motor, power a handheld calculator, or perform whatever other task we wish.

A large array of solar cells such as this can produce substantial amounts of electricity. *(Waltraud Grubitzsch/epa/© Corbis)*

Light-Emitting Diodes (LEDs)

A solar cell absorbs light energy and produces an electric current. If the process is reversed and an electric current is forced through the p-n junction in the opposite direction, light is emitted. A device using this process is called a **light-emitting diode (LED).** By an appropriate choice of materials, the color of the light can range across the visible spectrum. LEDs are used in a variety of applications, ranging from traffic lights to jumbo TV screens in sports stadiums.

DWYANE WADE
MVP

The jumbo TV screen in this sports stadium is made up of many light-emitting diodes. *(Juan Ó Campo/NBAEvia/Getty Images, Inc.)*

10.10 | Atomic Size and the Tendency toward Multiple Bond Formation

You learned earlier that the formation of a σ bond can involve the overlap of *s* orbitals, or an end-to-end overlap of *p* orbitals or hybrid orbitals (Figure 10.30, page 439). Formation of a π bond normally requires the sideways overlap of unhybridized *p* orbitals (Figure 10.31).[5]

The strengths of σ and π bonds depend on the sizes of the atoms involved—as atoms become larger, the bond strength generally decreases. In part, this is because the shared electrons are farther from the nuclei and are less effective at attracting them. Pi bonds are especially affected by atomic size. Small atoms, such as those in Period 2 of the periodic table, are able to approach each other closely. As a result, effective sideways overlap of their *p* orbitals can occur, and these atoms form strong π bonds. Atoms from Periods 3 through 6 are much larger and π-type overlap between their *p* orbitals is relatively ineffective, so π bonds formed by large atoms are relatively weak compared to σ bonds.

TOOLS
Tendency toward multiple bond formation

The effect of atomic size on the relative strengths of σ and π bonds leads to the following generalization: *Elements in Period 2 are able to form multiple bonds fairly readily, while elements below them in Periods 3, 4, 5, and 6 have a tendency to prefer single bonds.* The consequences of this generalization are particularly evident when we examine the complexity of the structures that occur for the elemental nonmetals.

Among the nonmetals, only the noble gases exist in nature as single atoms. All the others are found in more complex forms in their free states—some as diatomic molecules and the rest in more complex molecular structures.

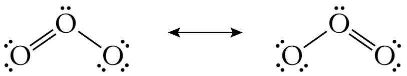
Nonmetals in Period 2

Fluorine (as well as the other halogens in Group 7A) has seven electrons in its outer shell and needs just one more electron to complete its valence shell. Fluorine is able to form the simple diatomic molecule F_2 with a single σ bond. The other halogens have similar formulas in their elemental states (Cl_2, Br_2, and I_2). Because only single bonds are involved, atomic size doesn't affect the complexity of the molecular structures of the halogens.

Moving to the left in the periodic table, the situation becomes more interesting for the elements in Groups 6A, 5A, and 4A. Oxygen and nitrogen have six and five electrons, respectively, in their valence shells. This means that an oxygen atom needs two electrons to complete its valence shell, and a nitrogen atom needs three. Oxygen and nitrogen, because of their small size, are capable of multiple bonding because they are able to form strong π bonds. This allows them to form a sufficient number of bonds with just a single neighbor to complete their valence shells, so they are able to form diatomic molecules.

The nitrogen molecule, which we discussed earlier, is able to complete its valence shell by forming a triple bond. Although a perfectly satisfactory Lewis structure for O_2 can't be drawn, experimental evidence suggests that the oxygen molecule does possess a double bond. Molecular orbital theory, which provides an excellent explanation of the bonding in O_2, also tells us that there is a double bond in the O_2 molecule.

Oxygen, in addition to forming the stable species O_2 (properly named *dioxygen*), also can exist in another very reactive molecular form called **ozone**, which has the formula O_3. The structure of ozone can be represented as a resonance hybrid,



This unstable molecule can be generated by the passage of an electric discharge through ordinary O_2, and the pungent odor of ozone can often be detected in the vicinity of high-voltage electrical equipment. It is also formed in limited amounts in the upper atmosphere by the action of ultraviolet radiation from the sun on O_2. The presence of ozone in the upper atmosphere shields earth and its life-forms from exposure to intense and harmful ultraviolet light from the sun.

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[5] Pi bonds can also be formed by *d* orbitals, but we do not discuss them in this book.

■ Ozone is also a component of photochemical smog formed by the interaction of sunlight with nitrogen oxides released in the exhaust of motor vehicles.

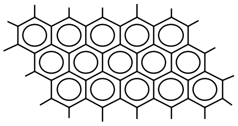
The existence of an element in more than one form, either as the result of differences in molecular structure as with O_2 and O_3, or as the result of differences in the packing of molecules in the solid, is a phenomenon called **allotropy**. The different forms of the element are called **allotropes**. Thus, O_2 is one allotrope of oxygen and O_3 is another. Allotropy is not limited to oxygen, as you will soon see.

Allotropes of Carbon

An atom of carbon, also a Period 2 element, has four electrons in its valence shell, so it must share four electrons to complete its octet. There is no way for carbon to form a quadruple bond, so a simple C_2 species is not stable under ordinary conditions. Instead, carbon completes its octet in other ways, leading to four allotropic forms of the element. One of these is **diamond**, in which each carbon atom uses sp^3 hybrid orbitals to form covalent bonds to four other carbon atoms at the corners of a tetrahedron (Figure 10.49*a*).

In its other allotropes, carbon employs sp^2 hybrid orbitals to form ring structures with delocalized π systems covering their surfaces. The most stable form of carbon is **graphite,** which consists of layers of carbon atoms, each composed of many hexagonal "benzene-like" rings fused together in a structure reminiscent of chicken wire. A single such layer is called **graphene** (see On the Cutting Edge 10.1). In graphene, a $2p$ orbital on each carbon atom forms a π-type of interaction with identical $2p$ orbitals on its neighbors.

■ The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov, both of the University of Manchester, England, for their discovery that individual layers of graphene could be isolated from graphite. Their discovery opened the door to an explosive growth in research on this very unusual material.



A fragment of a graphene layer in graphite.

In graphite, graphene layers are stacked one on top of another, as shown in Figure 10.49*b*. Graphite is an electrical conductor because of the delocalized π electron system that

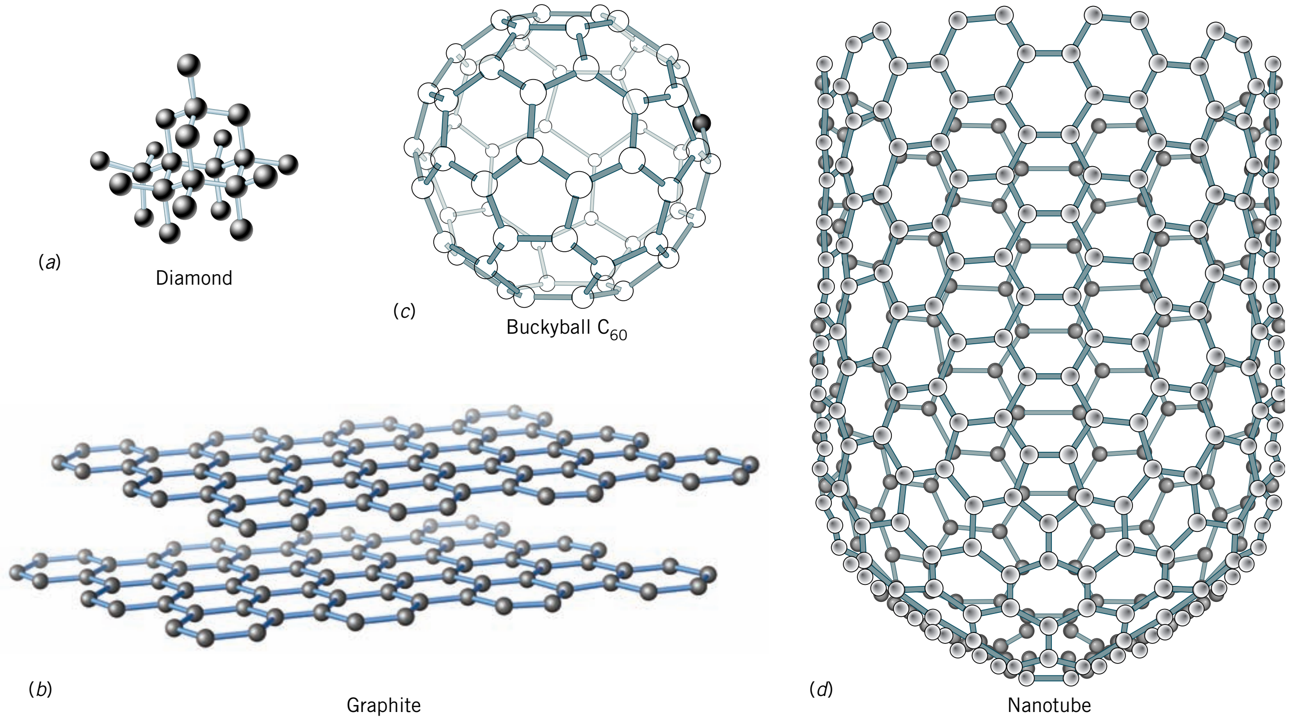


Figure 10.49 | **Molecular forms of carbon.** (*a*) Diamond. (*b*) Graphite. (*c*) Buckminsterfullerene, or "buckyball," C_{60}. (*d*) A portion of a carbon nanotube showing one closed end.

ON THE CUTTING EDGE 10.1

Graphene and the Future of Electronics

It has long been suspected that single layers of graphite, given the name *graphene* (Figure 1), would have surprising and potentially useful properties. However, difficulties in preparing graphene sheets by peeling them off crystals of graphite have prevented scientists from obtaining useful samples of the material, making accurate measurements impossible. These techniques yielded only small fragments of graphene.

Recently, scientists at IBM have developed a low-cost method of growing high-quality graphene on the surface of commercially available silicon carbide (SiC) wafers. Heating the wafers causes silicon to evaporate from the surface, and the carbon atoms left behind combine to form a graphene sheet.

Single sheets of graphene can transport electrons more quickly than other semiconductors, a property called *electron mobility*. The electron mobility of graphene, for example, is about 100 times greater than that of silicon, the semiconductor used in most currently available devices. For this reason, graphene is ideally suited for high-speed atomic scale operation. Furthermore, graphene's electrical properties can be controlled by switching it among conducting, nonconducting, and semiconducting states. This makes graphene a potential candidate for a variety of electronic devices.

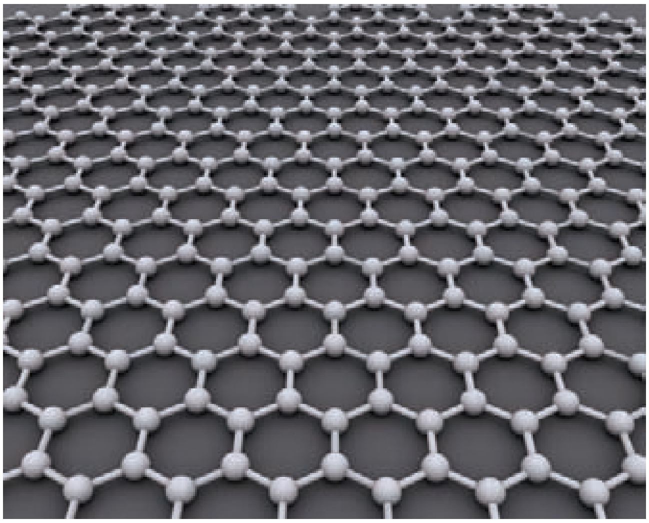


Figure 1. An illustration depicting a single graphene layer.

According to scientists at IBM, they have already created a graphene-based transistor with the capability of operating at speeds of 100 GHz, about three times as fast as a silicon-based processor. Such discoveries suggest that graphene may someday replace silicon in high-speed electronic circuits.

extends across the layers. Electrons can be pumped in at one end of a layer and removed from the other. Scientists have been able to isolate separate single layers of graphene, and there is much current interest in the physical and electrical properties of this carbon structure. For example, the breaking strength of graphene is more than 200 times that of steel!

In 1985, a new form of carbon was discovered that consists of tiny balls of carbon atoms, the simplest of which has the formula C_{60} (Figure 10.49*c*). They were named **fullerenes** and the C_{60} molecule itself was named **buckminsterfullerene** (nickname **buckyball**) in honor of R. Buckminster Fuller, the designer of a type of structure called a geodesic dome. The bonds between carbon atoms in the buckyball are arranged in a pattern of five- and six-membered rings arranged like the seams in a classic soccer ball, as well as the structural elements of the geodesic dome.

Carbon nanotubes, discovered in 1991, are another form of carbon that is related to the fullerenes. They are formed, along with fullerenes, when an electric arc is passed between carbon electrodes. The nanotubes consist of tubular carbon molecules that we can visualize as rolled-up sheets of graphene (with hexagonal rings of carbon atoms). The tubes are capped at each end with half of a spherical fullerene molecule, so a short tube would have a shape like a hot dog. A portion of a carbon nanotube is illustrated in Figure 10.49*d.* Carbon nanotubes have unusual properties that have made them the focus of much research in recent years.

■ Weight for weight, carbon nanotubes are about 100 times stronger than stainless steel and about 40 times stronger than the carbon fibers used to make tennis rackets and shafts for golf clubs.

Nonmetallic Elements below Period 2

In graphite, carbon exhibits multiple bonding, as do nitrogen and oxygen in their molecular forms. As we noted earlier, their ability to do this reflects their ability to form strong π bonds—a requirement for the formation of a double or triple bond. When we move to the third and successive periods, a different state of affairs exists. There, we have much larger atoms that are able to form relatively strong σ bonds but much weaker π bonds. Because their π bonds are so weak, these elements prefer single bonds (σ bonds), and the molecular structures of the free elements reflect this.

Elements of Group 6A

Below oxygen in Group 6A is sulfur, which has the Lewis symbol

$$:\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\cdot$$

A sulfur atom requires two electrons to complete its valence shell, so it must form two covalent bonds. However, sulfur doesn't form π bonds well to other sulfur atoms; instead, it prefers to form two stronger single bonds to *different* sulfur atoms. Each of these also prefers to bond to two different sulfur atoms, and this gives rise to a

$$-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}-$$

sequence. Actually, in sulfur's most stable form, called **orthorhombic sulfur**, the sulfur atoms are arranged in an eight-member ring to give a molecule with the formula S_8 (properly named *cyclooctasulfur*). The S_8 ring has a puckered crown-like shape, which is illustrated in Figure 10.50. Another allotrope is **monoclinic sulfur,** which also contains S_8 rings that are arranged in a slightly different crystal structure.

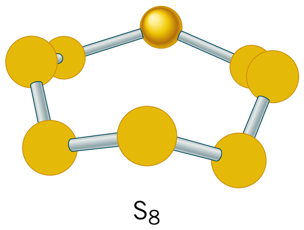


Figure 10.50 | **The structure of the puckered S_8 ring.**

When solid sulfur is heated, it undergoes some interesting changes (Figure 10.51). When the solid first melts, the liquid that forms consists of S_8 molecules. As the liquid is heated further, the rings begin to open into chains of sulfur atoms that join to form long strands. The strands of sulfur atoms become intertwined, causing the liquid to become very viscous. Further heating causes the strands of sulfur to break into smaller fragments, and when the liquid boils it is no longer viscous.

Selenium, below sulfur in Group 6A, also forms Se_8 rings in one of its allotropic forms. Both selenium and tellurium also can exist in a gray form in which there are long Se_x and Te_x chains (where the subscript x is a large number).

Elements of Group 5A

Like nitrogen, the other elements in Group 5A all have five valence electrons. Phosphorus is an example:

$$:\overset{\cdot}{\underset{\cdot}{\mathrm{P}}}\cdot$$

To achieve a noble gas structure, the phosphorus atom must acquire three more electrons. Because there is little tendency for phosphorus to form multiple bonds, as nitrogen does when it forms N_2, the octet is completed by the formation of three single bonds to three *different* phosphorus atoms.

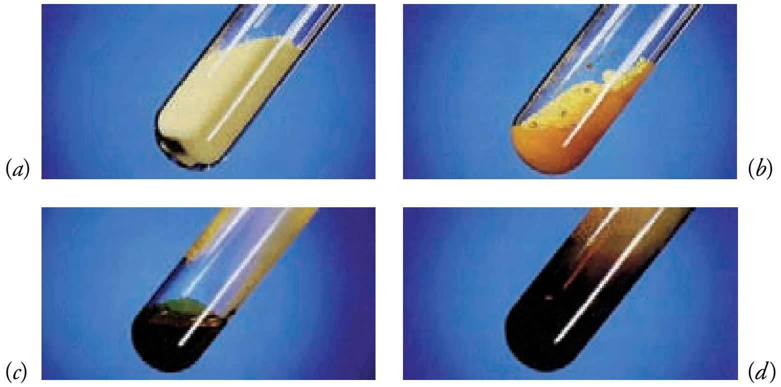


Figure 10.51 | **Changes in sulfur as it is heated.** (*a*) Crystalline sulfur. (*b*) Molten sulfur just above its melting point. (*c*) Molten sulfur, just below 200 °C, is dark and viscous. (*d*) Boiling suflur is dark red and no longer viscous. *(Michael Watson)*

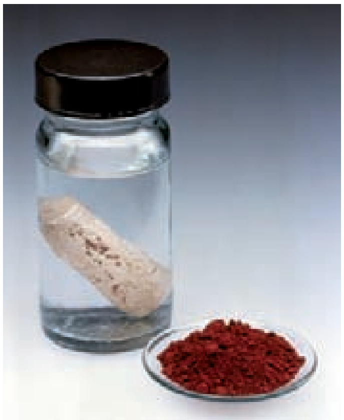


Figure 10.52 | **The two main allotropes of phosphorus.** (*a*) White phosphorus. (*b*) Red phosphorus. *(Richard Megna/Fundamental Photographs)*

■ The preferred angle between bonds formed by *p* orbitals is 90°. Each face of the P_4 tetrahedron is a triangle, however, with 60° angles between edges. This produces less than optimum overlap between the *p* orbitals in the bonds.

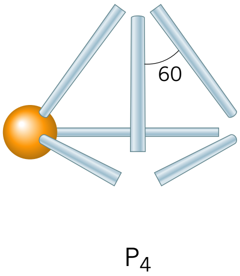


Figure 10.53 | **The molecular structure of white phosphorus, P_4.** The bond angles of 60° makes the phosphorus–phosphorus bonds quite weak and causes the molecule to be very reactive.

The simplest elemental form of phosphorus is a waxy solid called **white phosphorus** because of its appearance (Figure 10.52). It consists of P_4 molecules in which each phosphorus atom lies at a corner of a tetrahedron, as illustrated in Figure 10.53. Notice that in this structure each phosphorus is bound to three others. This allotrope of phosphorus is very reactive, partly because of the very small P—P—P bond angle of 60°. At this small angle, the *p* orbitals of the phosphorus atoms don't overlap very well, so the bonds are weak. As a result, breaking a P—P bond occurs easily. When a P_4 molecule reacts, this bond breaking is the first step, so P_4 molecules are readily attacked by other chemicals, especially oxygen. White phosphorus is so reactive toward oxygen that it ignites and burns spontaneously in air. For this reason, white phosphorus is used in military incendiary devices, and you've probably seen movies in which exploding phosphorus shells produce arching showers of smoking particles.

A second allotrope of phosphorus that is much less reactive is called **red phosphorus**. At the present time, its structure is unknown, although it has been suggested that it contains P_4 tetrahedra joined at the corners as shown in Figure 10.54. Red phosphorus is also used in explosives and fireworks, and it is mixed with fine sand and used on the striking surfaces of matchbooks. As a match is drawn across the surface, friction ignites the phosphorus, which then ignites the ingredients in the tip of the match.

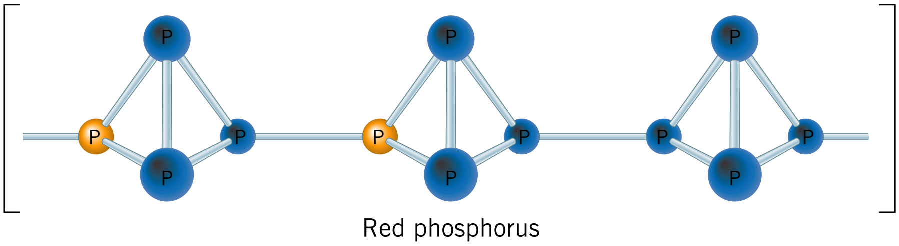
A third allotrope of phosphorus is called **black phosphorus**, which is formed by heating white phosphorus at very high pressures. This variety has a layered structure in which each phosphorus atom in a layer is covalently bonded to three others in the same layer. As in graphite, these layers are stacked one atop another, with only weak forces between the layers. As you might expect, black phosphorus has many similarities to graphite.

The elements arsenic and antimony, which are just below phosphorus in Group 5A, are also able to form somewhat unstable yellow allotropic forms containing As_4 and Sb_4 molecules, but their most stable forms have a metallic appearance with structures similar to black phosphorus.

Elements of Group 4A

Finally, we look at silicon and germanium, the heavier nonmetallic elements in Group 4A. To complete their octets, each must form four covalent bonds. Unlike carbon, however, they have very little tendency to form multiple bonds, so they don't form allotropes that have a graphite structure. Instead, each of them forms a solid with a structure similar to diamond.

Figure 10.54 | **Proposed molecular structure of red phosphorus.** Red phosphorus is believed to be composed of long chains of P_4 tetrahedra connected at their corners.



Summary

Molecular Shapes and the VSEPR Model. The structures of most molecules can be described in terms of one or another of five basic geometries: **linear, planar triangular, tetrahedral, trigonal bipyramidal,** and **octahedral**. The **VSEPR theory** predicts molecular geometry by assuming that **electron domains**—regions of space that contain bonding electrons, unpaired valence electrons, or lone pairs—stay as far apart as possible from each other, while staying as close as possible to the central atom. Figures 10.4, 10.5, 10.7, and 10.10 illustrate the structures obtained with different numbers of groups of electrons in the valence shell of the central atom in a molecule or ion and with different numbers of lone pairs and attached atoms. The correct shape of a molecule or polyatomic ion can usually be predicted from the Lewis structure.

Molecular Shape and Molecular Polarity. A molecule that contains identical atoms attached to a central atom will be nonpolar if there are no lone pairs of electrons in the central atom's valence shell. It will be polar if lone pairs are present, except in two cases: (1) when there are three lone pairs and two attached atoms, and (2) when there are two lone pairs and four attached atoms. If all the atoms attached to the central atom are not alike, the molecule will usually be polar.

Valence Bond (VB) Theory. According to VB theory, a covalent bond is formed between two atoms when an atomic orbital on one atom **overlaps** with an atomic orbital on the other and a pair of electrons with paired spins is shared between the overlapping orbitals. In general, the better the overlap of the orbitals, the stronger the bond. A given atomic orbital can overlap only with one other orbital on a different atom, so a given atomic orbital can only form one bond with an orbital on one other atom.

Hybrid Atomic Orbitals. **Hybrid orbitals** are formed by mixing pure *s*, *p*, and *d* orbitals. Hybrid orbitals overlap better with other orbitals than the pure atomic orbitals from which they are formed, so bonds formed by hybrid orbitals are stronger than those formed by ordinary atomic orbitals. **Sigma bonds** (σ bonds) are formed by the following kinds of orbital overlap: *s*–*s*, *s*–*p*, end-to-end *p*–*p*, and overlap of hybrid orbitals. Sigma bonds allow free rotation around the bond axis. The side-by-side overlap of *p* orbitals produces a **pi bond** (π bond). Pi bonds do not permit free rotation around the bond axis because such a rotation involves bond breaking. In complex molecules, the basic molecular framework is built with σ bonds. A double bond consists of one σ bond and one π bond. A triple bond consists of one σ bond and two π bonds.

Molecular Orbital (MO) Theory. MO theory begins with the supposition that molecules are similar to atoms, except that they have more than one positive center. They are treated as collections of nuclei and electrons, with the electrons of the molecule distributed among **molecular orbitals** of different energies. Molecular orbitals can spread over two or more nuclei, and can be considered to be formed by the constructive and destructive interference of the overlapping electron waves corresponding to the atomic orbitals of the atoms in the molecule. **Bonding MOs** concentrate electron density between nuclei; **antibonding MOs** remove electron density from between nuclei. **Nonbonding MOs** do not affect the energy of the molecule. The rules for the filling of MOs are the same as those for atomic orbitals. The ability of MO theory to describe **delocalized orbitals** avoids the need for resonance theory. Delocalization of bonds leads to a lowering of the energy by an amount called the **delocalization energy** and produces more stable molecular structures.

Band Theory of Solids. In solids, atomic orbitals of the atoms combine to yield **energy bands** that consist of many energy levels. The **valence band** is formed by orbitals of the valence shells of the atoms. A **conduction band** is a partially filled or empty band. In an **electrical conductor** the conduction band is either partially filled or is empty and overlaps a filled band. In an **insulator**, the **band gap** between the filled valence band and the empty conduction band is large, so no electrons populate the conduction band. In a **semiconductor**, the band gap between the filled valence band and the conduction band is small and thermal energy can promote some electrons to the conduction band. Silicon becomes a **p-type semiconductor**, in which the charge is carried by positive **"holes,"** if it is **doped** with a Group 3A element such as boron. It becomes an **n-type semiconductor**, in which the charge is carried by electrons, if it is doped with a Group 5A element such as arsenic.

Tendency toward Multiple Bond Formation. Elements of Period 2, because of their small size, form strong π bonds. As a result, these elements easily participate in multiple bonding between like atoms, which accounts for diatomic molecules of O_2 and N_2, and the π-bonded structure of **graphene**. Elements of Periods 3, 4, and 5 are large and their *p* orbitals do not overlap well to form strong π bonds, so these elements prefer single σ bonds between like atoms, which leads to more complex molecular structures.

Different forms of the same element are called **allotropes**. Oxygen exists in two allotropic forms: dioxygen (O_2) and **ozone** (O_3). Carbon forms several allotropes, including **diamond, graphite** (composed of layers of graphene), C_{60} molecules called **buckminsterfullerene** (one member of the **fullerene** family of structures), and **carbon nanotubes**. Sulfur forms S_8 molecules that can be arranged in two different allotropic forms. Phosphorus occurs as **white phosphorus** (P_4), **red phosphorus**, and **black phosphorus**. Silicon only forms a diamond-like structure.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so that you can select the appropriate tool when needed.

Basic molecular shapes (pages 409)
You need an understanding of the five basic geometries discussed. Practice drawing them and be sure you know their names.

VSEPR model (page 411)
Electron groups repel each other and arrange themselves in the valence shell of an atom to yield minimum repulsions, which is what determines the shape of the molecule. This tool serves as the foundation for understanding the VSEPR model.

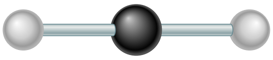
Applying the VSEPR model (page 417)
To obtain a molecular structure, follow these steps: (1) draw the Lewis structure, (2) count electron domains, (3) select the basic geometry, (4) add atoms to bonding domains, and (5) ignore nonbonding domains to describe the shape.

Molecular shape and molecular polarity (page 422)
We can use molecular shape to determine whether a molecule will be polar or nonpolar. Refer to the summary on page 422.

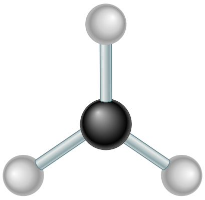
Criteria for bond formation according to VB theory (page 424)
A bond requires overlap of two orbitals sharing two electrons with paired spins. Both orbitals can be half-filled, or one can be filled and the other empty. We use these criteria to establish which orbitals atoms use when bonds are formed.

Hybrid orbitals formed by *s* and *p* atomic orbitals (page 430)
The orientations of these hybrids are the same as those predicted for two, three, and four electron domains.

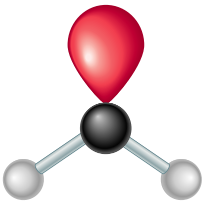
The VSEPR model and hybrid orbitals involving *s* and *p* electrons (page 432)
These tools are interrelated. Lewis structures permit us to use the VSEPR model to predict molecular shape, which then allows us to select the correct hybrid orbitals for the valence bond description of bonding. After forming the Lewis structure, we determine the number of domains, from which we derive the structure of the molecule or ion. A convenient way of doing this is to describe the VSEPR structure symbolically. In doing this we represent the central atom by M, the atoms attached to the central atom by X, and lone pairs by E. We can then signify the number of bonding and nonbonding domains around M as a formula MX_nE_m, where n is the number of bonding domains and m is the number of nonbonding domains. The resulting formula is related to the structure of the molecule or ion, and to the hybrid orbitals used by the central atom, as shown below. Practice sketching the structures, associating them with the appropriate generalized formula MX_nE_m, and using the structures to select the appropriate set of hybrid orbitals. The following structures are obtained for two, three, and four domains.



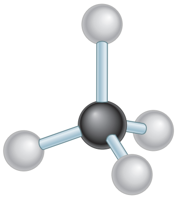
MX_2
sp
Linear



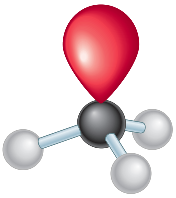
MX_3
sp^2
Planar triangular



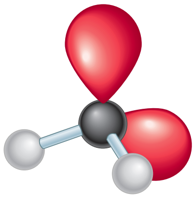
MX_2E
sp^2
Nonlinear (bent)



MX_4
sp^3
Tetrahedral



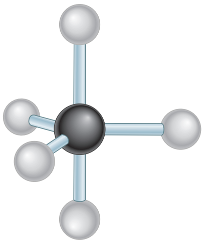
MX_3E
sp^3
Trigonal pyramidal



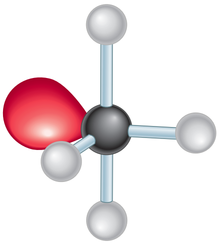
MX_2E_2
sp^3
Nonlinear (bent)

The VSEPR model and hybrid orbitals involving *d* electrons (page 434)

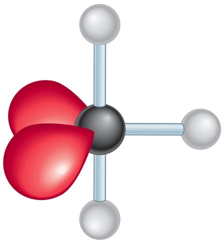
As with the preceding tool, we form the Lewis structure, count bonding and nonbonding domains and select the structure. The following structures are obtained for five and six domains using the generalized formula MX_nE_m.



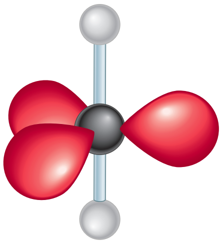
MX_5
sp^3d
Trigonal bipyramidal



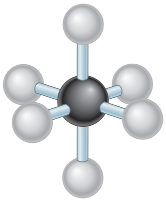
MX_4E
sp^3d
Seesaw or distorted tetrahedral



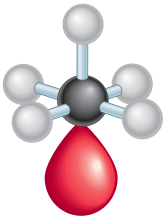
MX_3E_2
sp^3d
T-shaped



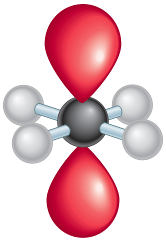
MX_2E_3
sp^3d
Linear



MX_6
sp^3d^2
Octahedral



MX_5E
sp^3d^2
Square pyramidal



MX_4E_2
sp^3d^2
Square planar

σ and π bonds and hybridization (page 433)

The Lewis structure for a polyatomic molecule lets us apply these criteria to determine how many σ and π bonds are between atoms and the kind of hybrid orbitals each atom uses. Remember that the shape of the molecule is determined by the framework of σ bonds, with π bonds used in double and triple bonds.

Calculating bond order in MO theory (page 447)

$$\text{Bond order} = \frac{(\text{number of bonding } e^-) - (\text{number of antibonding } e^-)}{2 \text{ electrons/bond}}$$

How electrons fill molecular orbitals (page 448)

Electrons populate MOs following the same rules that apply to atomic orbitals in an atom. Use this tool to obtain the correct distribution of electrons over the MOs of a molecule or ion.

Tendency toward multiple bond formation (page 456)

Atoms of Period 2 have a stronger tendency to form multiple bonds with each other than do those in Periods 3 and below.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Shapes of Molecules

10.1 Sketch the following molecular shapes and give the various bond angles in the structures: **(a)** planar triangular, **(b)** tetrahedral, **(c)** octahedral.

10.2 Sketch the following molecular shapes and give the bond angles in the structures: **(a)** linear, **(b)** trigonal bipyramidal.

VSEPR Theory

10.3 What is the underlying principle on which the VSEPR model is based?

10.4 What is an electron domain?

10.5 How many bonding domains and how many nonbonding domains are there in a molecule of formaldehyde, HCHO?

10.6 Sketch the following molecular shapes and give the various bond angles in the structure: **(a)** T-shaped, **(b)** seesaw shaped, and **(c)** square pyramidal.

10.7 What arrangements of domains around an atom are expected when there are **(a)** three domains, **(b)** six domains, **(c)** four domains, or **(d)** five domains?

Predicting Molecular Polarity

10.8 Why is it useful to know the polarities of molecules?

10.9 How do we indicate a bond dipole when we draw the structure of a molecule?

10.10 Under what conditions will a molecule be polar?

10.11 What condition must be met if a molecule having polar bonds is to be nonpolar?

10.12 Use a drawing to show why the SO_2 molecule is polar.

Modern Bonding Theories

10.13 What is the theoretical basis of both valence bond (VB) theory and molecular orbital (MO) theory?

10.14 What shortcomings of Lewis structures and VSEPR theory do VB and MO theories attempt to overcome?

10.15 What is the main difference in the way VB and MO theories view the bonds in a molecule?

Valence Bond Theory

10.16 What is meant by orbital overlap?

10.17 How is orbital overlap related to bond energy?

10.18 Use sketches of orbitals to describe how VB theory would explain the formation of the H—Br bond in hydrogen bromide.

Hybrid Orbitals

10.19 Why do atoms usually use hybrid orbitals for bonding rather than pure atomic orbitals?

10.20 Sketch figures that illustrate the directional properties of the following hybrid orbitals: **(a)** sp, **(b)** sp^2, **(c)** sp^3.

10.21 Sketch figures that illustrate the directional properties of the following hybrid orbitals: **(a)** sp^3d, **(b)** sp^3d^2.

10.22 Why do Period 2 elements never use sp^3d or sp^3d^2 hybrid orbitals for bond formation?

10.23 What relationship is there, if any, between Lewis structures and the valence bond descriptions of molecules?

10.24 How can the VSEPR model be used to predict the hybridization of an atom in a molecule?

10.25 If the central oxygen in the water molecule did not use sp^3 hybridized orbitals (or orbitals of any other kind of hybridization), what would be the expected bond angle in H_2O?

10.26 Using orbital diagrams, describe how sp^3 hybridization occurs in each atom: **(a)** carbon, **(b)** nitrogen, **(c)** oxygen. If these elements use sp^3 hybrid orbitals to form bonds, how many lone pairs of electrons would be found on each?

10.27 Sketch the way the orbitals overlap to form the bonds in each of the following: **(a)** CH_4, **(b)** NH_3, **(c)** H_2O. (Assume the central atom uses hybrid orbitals.)

10.28 We explained the bond angles of 107° in NH_3 by using sp^3 hybridization of the central nitrogen atom. If unhybridized p orbitals of nitrogen were used to overlap with $1s$ orbitals of each hydrogen, what would the H—N—H bond angles be? Explain.

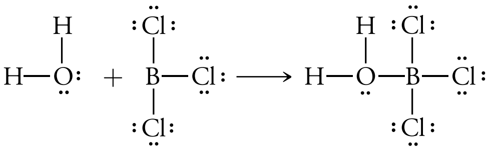
10.29 Using sketches of orbitals and orbital diagrams, describe sp^2 hybridization of **(a)** boron and **(b)** carbon.

10.30 What two basic shapes have hybridizations that include d orbitals?

Coordinate Covalent Bonds and VB Theory

10.31 The ammonia molecule, NH_3, can combine with a hydrogen ion, H^+ (which has an empty $1s$ orbital), to form the ammonium ion, $NH_4{}^+$. (This is how ammonia can neutralize acid and therefore function as a base.) Sketch the geometry of the ammonium ion, indicating the bond angles.

10.32 How does the geometry around B and O change in the following reaction? How does the hybridization of each atom change?



Multiple Bonds and Hybrid Orbitals

10.33 How do σ and π bonds differ?

10.34 Why can free rotation occur easily around a σ-bond axis but not around a π-bond axis?

10.35 Using sketches, describe the bonds and bond angles in ethene, C_2H_4.

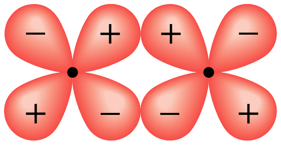
10.36 Sketch the way the bonds form in acetylene, C_2H_2.

10.37 How does VB theory treat the benzene molecule? (Draw sketches describing the orbital overlaps and the bond angles.)

Molecular Orbital Theory

10.38 Why is the higher-energy MO in H_2 called an *antibonding orbital*? Make a sketch of the bonding and antibonding orbitals in H_2.

10.39 Below is an illustration showing two 3*d* orbitals about to overlap. The drawings also show the algebraic signs of the wave functions for both orbitals in this combination. Will this combination of orbitals produce a bonding or an antibonding MO? Sketch the shape of the MO.



10.40 Will the combination of 3*d* orbitals in Question 10.39 yield a σ- or π-type of MO? Explain.

10.41 Explain why He_2 does not exist but H_2 does.

10.42 How does MO theory account for the paramagnetism of O_2?

10.43 On the basis of MO theory, explain why Li_2 molecules can exist but Be_2 molecules cannot. Could the ion $Be_2{}^+$ exist?

10.44 What are the bond orders in **(a)** $O_2{}^+$, **(b)** $O_2{}^-$, and **(c)** $C_2{}^+$?

10.45 What relationship is there between bond order and bond energy?

10.46 Sketch the shapes of the π_{2p_y} and $\pi^*_{2p_y}$ MOs.

10.47 What is a delocalized MO? Explain, in terms of orbital overlap, why delocalized MOs are able to form in the benzene molecule.

10.48 What effect does delocalization have on the stability of the electronic structure of a molecule?

10.49 What is delocalization energy? How is it related to resonance energy?

Band Theory of Solids

10.50 On the basis of the band theory of solids, how do conductors, insulators, and semiconductors differ?

10.51 Define the terms **(a)** *valence band* and **(b)** *conduction band*.

10.52 Why does the electrical conductivity of a semiconductor increase with increasing temperature?

10.53 In calcium, why can't electrical conduction take place by movement of electrons through the 2*s* energy band? How does calcium conduct electricity?

10.54 What is a p-type semiconductor? What is an n-type semiconductor?

10.55 Name two elements that would make germanium a p-type semiconductor when added in small amounts. Name two elements that would make silicon an n-type semiconductor when added in small amounts.

10.56 How does a solar cell work? How does that differ from the operation of a light-emitting diode?

Tendency toward Multiple Bond Formation

10.57 Which of the nonmetals occur in nature in the form of isolated atoms?

10.58 Why are the Period 2 elements able to form much stronger π bonds than the nonmetals of Period 3? Why does a Period 3 nonmetal prefer to form all σ bonds instead of one σ bond and several π bonds?

10.59 Even though the nonmetals of Periods 3, 4, and 5 do not tend to form π bonds between like atoms, each of the halogens is able to form diatomic molecules (Cl_2, Br_2, I_2). Why?

10.60 What are *allotropes*? How do they differ from *isotopes*?

10.61 What are the two allotropes of oxygen?

10.62 Construct the molecular orbital diagram for O_2. What is the net bond order in O_2?

10.63 Draw the Lewis structure for O_3. Is the molecule linear, based on the VSEPR model? Assign formal charges to the atoms in the Lewis structure. Does this suggest the molecule is polar or nonpolar?

10.64 What beneficial function does ozone serve in earth's upper atmosphere?

10.65 Describe the structure of diamond. What kind of hybrid orbitals does carbon use to form bonds in diamond? What is the geometry around carbon in this structure?

10.66 Describe the structure of graphene. What kind of hybrid orbitals does carbon use in the formation of the molecular framework of graphene?

10.67 How is the structure of graphite related to the structure of graphene?

10.68 Describe the C_{60} molecule. What is it called? What name is given to the series of similar substances?

10.69 How is the structure of a carbon nanotube related to the structure of graphene?

10.70 What is the molecular structure of sulfur in its most stable allotropic form?

10.71 Make a sketch that describes the molecular structure of white phosphorus.

10.72 What are the P—P—P bond angles in the P_4 molecule? If phosphorus uses *p* orbitals to form the phosphorus–phosphorus bonds, what bond angle would give the best orbital overlap? On the basis of your answers to these two questions, explain why P_4 is so chemically reactive.

10.73 What structure has been proposed for red phosphorus? How do the reactivities of red and white phosphorus compare?

10.74 What is the molecular structure of black phosphorus? In what way does the structure of black phosphorus resemble that of graphite?

10.75 What is the molecular structure of silicon? Suggest a reason why silicon doesn't form an allotrope that's similar in structure to graphite?

Review Problems

The VSEPR model

10.76 Predict the shapes of **(a)** NH_2^-, **(b)** CO_3^{2-}, **(c)** IF_3, **(d)** Br_3^-, and **(e)** GaH_3.

10.77 Predict the shapes of **(a)** SF_3^+, **(b)** GeF_4, **(c)** SO_4^{2-}, **(d)** O_3, and **(e)** N_2O.

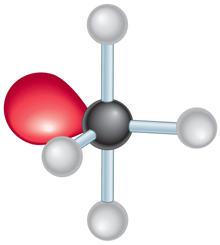
ILW **10.78** Predict the shapes of **(a)** FCl_2^+, **(b)** AsF_5, **(c)** AsF_3, **(d)** SbH_3, and **(e)** SeO_2.

10.79 Predict the shapes of **(a)** TeF_4, **(b)** $SbCl_6^-$, **(c)** NO_2^-, **(d)** PCl_4^+, and **(e)** PO_4^{3-}.

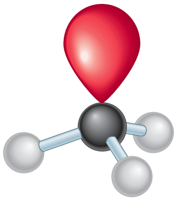
10.80 Predict the shapes of **(a)** IO_4^-, **(b)** IF_4^-, **(c)** TeF_6, **(d)** SiO_4^{4-}, and **(e)** ICl_2^-.

10.81 Predict the shapes of **(a)** CS_2, **(b)** BrF_4^-, **(c)** ICl_3, **(d)** ClO_3^-, and **(e)** SeO_3.

10.82 Which of the following has a shape described by the figure below: **(a)** IO_4^-, **(b)** ICl_4^-, **(c)** $SnCl_4$, or **(d)** BrF_4^+?

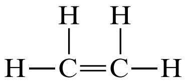


10.83 Which of the following has a shape described by the figure below: **(a)** BrF_3, **(b)** PF_3, **(c)** NO_3^-, or **(d)** SCl_3^-?



10.84 Ethyne, more commonly called acetylene, is a gas used in welding torches. It has the Lewis structure H—C≡C—H. What would you expect the H—C—C bond angle to be in this molecule?

OH **10.85** Ethene, also called ethylene, is a gas used to ripen tomatoes artificially. It has the Lewis structure



$$\begin{array}{c} \mathrm{H}\quad\mathrm{H} \\ |\quad\;\; | \\ \mathrm{H{-}C{=}C{-}H} \end{array}$$

What would you expect the H—C—H and H—C═C bond angles to be in this molecule? (*Caution:* Don't be fooled by the way the structure is drawn here.)

10.86 Predict the bond angle for each of the following molecules: **(a)** Cl_2O, **(b)** H_2O, **(c)** SO_2, **(d)** I_3^-, **(e)** NH_2^-.

10.87 Predict the bond angle for each of the following molecules: **(a)** HOCl, **(b)** PH_2^-, **(c)** OCN^-, **(d)** O_3, **(e)** SnF_2.

Predicting Molecular Polarity

ILW **10.88** Which of the following molecules would be expected to be polar? **(a)** HBr, **(b)** $POCl_3$, **(c)** CH_2O, **(d)** $SnCl_4$, **(e)** $SbCl_5$

10.89 Which of the following molecules would be expected to be polar? **(a)** PBr_3, **(b)** SO_3, **(c)** $AsCl_3$, **(d)** ClF_3, **(e)** BCl_3

10.90 Which of the following molecules or ions would be expected to have a net dipole moment? **(a)** ClNO, **(b)** XeF_3^+, **(c)** $SeBr_4$, **(d)** NO, **(e)** NO_2

10.91 Which of the following molecules or ions would be expected to have a net dipole moment? **(a)** H_2S, **(b)** BeH_2, **(c)** SCN^-, **(d)** CN^-, **(e)** $BrCl_3$

OH **10.92** Explain why SF_6 is nonpolar, but SF_5Br is polar.

10.93 Explain why CH_3Cl is polar, but CCl_4 is not.

Valence Bond Theory

10.94 Hydrogen selenide is one of nature's most foul-smelling substances. Molecules of H_2Se have H—Se—H bond angles very close to 90°. How would VB theory explain the bonding in H_2Se? Use sketches of orbitals to show how the bonds are formed. Illustrate with appropriate orbital diagrams as well.

OH **10.95** Use sketches of orbitals to show how VB theory explains the bonding in the Cl_2 molecule. Illustrate with appropriate orbital diagrams as well.

Hybrid Orbitals

10.96 Use orbital diagrams to explain how the beryllium chloride molecule is formed. What kind of hybrid orbitals does beryllium use in this molecule?

10.97 Use orbital diagrams to describe the bonding in **(a)** tin tetrachloride and **(b)** antimony pentachloride. Be sure to indicate hybrid orbital formation.

OH **10.98** Draw Lewis structures for the following and use the geometry predicted by the VSEPR model to determine what kind of hybrid orbitals the central atom uses in bond formation: **(a)** ClO_3^-, **(b)** SO_3, and **(c)** OF_2.

10.99 Draw Lewis structures for the following and use the geometry predicted by the VSEPR model to determine what kind of hybrid orbitals the central atom uses in bond formation: **(a)** $SbCl_6^-$, **(b)** PF_3, and **(c)** XeF_4.

10.100 Use the VSEPR model to help you describe the bonding in the following molecules according to VB theory: **(a)** arsenic trichloride and **(b)** chlorine trifluoride. Use orbital diagrams for the central atom to show how hybridization occurs.

10.101 Use the VSEPR model to help you describe the bonding in the following molecules according to VB theory: **(a)** antimony trichloride and **(b)** selenium dichloride. Use orbital diagrams for the central atom to show how hybridization occurs.

Coordinate Covalent Bonds and VB Theory

10.102 Use orbital diagrams to show that the bonding in SbF_6^- involves the formation of a coordinate covalent bond.

10.103 What kind of hybrid orbitals are used by tin in $SnCl_6^{2-}$? Draw the orbital diagram for Sn in $SnCl_6^{2-}$. What is the geometry of $SnCl_6^{2-}$?

Multiple Bonding and Valence Bond Theory

10.104 A nitrogen atom can undergo sp^2 hybridization when it becomes part of a carbon–nitrogen double bond, as in $H_2C{=}NH$.

(a) Using a sketch, show the electron configuration of sp^2 hybridized nitrogen just before the overlapping occurs to make this double bond.

(b) Using sketches (and the analogy to the double bond in C_2H_4), describe the two bonds of the carbon–nitrogen double bond.

(c) Describe the geometry of $H_2C{=}NH$ (using a sketch that shows all expected bond angles).

10.105 A nitrogen atom can undergo *sp* hybridization and then become joined to carbon by a triple bond to give the structural unit $-C{\equiv}N{:}$. This triple bond consists of one σ bond and two π bonds.

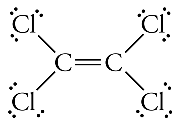
(a) Write the orbital diagram for *sp* hybridized nitrogen as it would look before any bonds form.

(b) Using the carbon–carbon triple bond as the analogy and drawing pictures to show which atomic orbitals overlap with which, show how the three bonds of the triple bond in $-C{\equiv}N{:}$ form.

(c) Again using sketches, describe all the bonds in hydrogen cyanide, $H{-}C{\equiv}N{:}$.

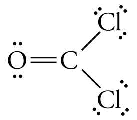
(d) What is the likeliest H—C—N bond angle in HCN?

10.106 Tetrachloroethylene, a common dry-cleaning solvent, has the formula C_2Cl_4. Its structure is



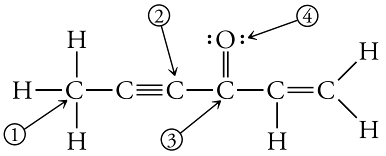
Use the VSEPR and VB theories to describe the bonding in this molecule. What are the expected bond angles in the molecule?

10.107 Phosgene, $COCl_2$, was used as a war gas during World War I. It reacts with moisture in the lungs of its victims to form CO_2 and gaseous HCl, which cause the lungs to fill with fluid. Phosgene is a simple molecule having the structure

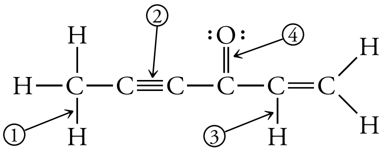


Describe the bonding in this molecule using VB theory.

10.108 What kind of hybrid orbitals do the numbered atoms use in the following molecule?



OH **10.109** What kinds of bonds (σ, π) are found in the numbered bonds in the following molecule?



Molecular Orbital Theory

OH ILW **10.110** Use the MO energy diagram to predict which in each pair has the greater bond energy: **(a)** O_2 or O_2^+, **(b)** O_2 or O_2^-, **(c)** N_2 or N_2^+.

10.111 Assume that in the NO molecule the molecular orbital energy level sequence is similar to that for O_2. What happens to the NO bond length when an electron is removed from NO to give NO^+? How would the bond energy of NO compare to that of NO^+?

10.112 In each of the following pairs, which substance has the longer bond length? **(a)** N_2 or N_2^+, **(b)** NO or NO^+, **(c)** O_2 or O_2^-

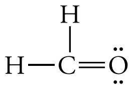
10.113 Which of the following molecules or ions are paramagnetic? **(a)** O_2^+, **(b)** O_2, **(c)** O_2^-, **(d)** NO, **(e)** N_2

10.114 Construct the MO energy level diagram for the OH molecule assuming it is similar to that for HF. How many electrons are in **(a)** bonding MOs and **(b)** nonbonding MOs? What is the net bond order in the molecule?

10.115 If boron and nitrogen were to form a molecule with the formula BN, what would its MO energy level diagram look like, given that the energies of the 2*p* orbitals of nitrogen are lower than those of boron. If Figure 10.38*a* applies, would the molecule be paramagnetic or diamagnetic? What is the net bond order in the molecule?

Additional Exercises

OH **10.116** Formaldehyde has the Lewis structure



$$H-\overset{\overset{\displaystyle H}{|}}{C}=\ddot{\underset{\cdot\cdot}{O}}$$

What would you predict its shape to be?

10.117 The molecule XCl_3 is pyramidal. In which group in the periodic table is element *X* found? If the molecule were planar triangular, in which group would *X* be found? If the molecule were T-shaped, in which group would *X* be found? Why is it unlikely that element *X* is in Group 6A?

10.118 Antimony forms a compound with hydrogen that is called stibine. Its formula is SbH_3 and the H—Sb—H bond angles are 91.3°. Which kinds of orbitals does Sb most likely use to form the Sb—H bonds: pure *p* orbitals or hybrid orbitals? Explain your reasoning.

10.119 Describe the changes in molecular geometry and hybridization that take place during the following reactions:

(a) $BF_3 + F^- \longrightarrow BF_4^-$

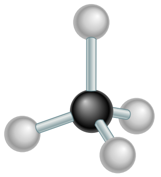
(b) $PCl_5 + Cl^- \longrightarrow PCl_6^-$

(c) $ICl_3 + Cl^- \longrightarrow ICl_4^-$

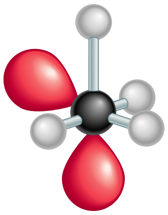
(d) $2PCl_3 + Cl_2 \longrightarrow PCl_5$

(e) $C_2H_2 + H_2 \longrightarrow C_2H_4$

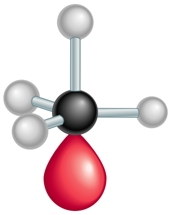
10.120 Which one of the following five diagrams best represents the structure of $BrCl_4^+$?



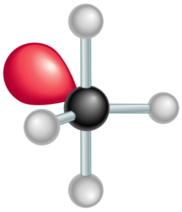
(a)



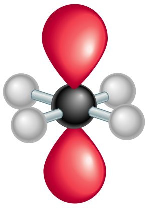
(b)



(c)

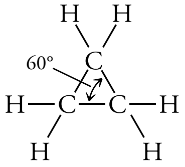


(d)

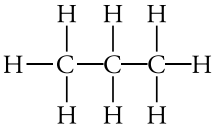


(e)

OH **10.121** Cyclopropane is a triangular molecule with C—C—C bond angles of 60°. Explain why the σ bonds joining carbon atoms in cyclopropane are weaker than the carbon–carbon σ bonds in the noncyclic propane.



cyclopropane



propane

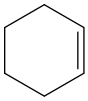
10.122 Phosphorus trifluoride, PF_3, has F—P—F bond angles of 97.8°.

(a) How would VB theory use hybrid orbitals to explain these data?

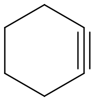
(b) How would VB theory use unhybridized orbitals to account for these data?

(c) Do either of these models work very well?

10.123 A six-membered ring of carbons can hold a double bond but not a triple bond. Explain.



cyclohexene (exists)



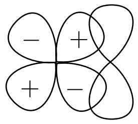
cyclohexyne (unknown)

***10.124** *The more electronegative are the atoms bonded to the central atom, the less are the repulsions between the electron pairs in the bonds.* On the basis of this statement, predict the most probable structure for the molecule PCl_3F_2. Do we expect the molecule to be polar or nonpolar?

***10.125** *A lone pair of electrons in the valence shell of an atom has a larger effective volume than a bonding electron pair. Lone pairs therefore repel other electron pairs more strongly than do bonding pairs.* On the basis of these statements, describe how the bond angles in TeF_4 and BrF_5 deviate from those found in a trigonal bipyramid and an octahedron, respectively. Sketch the molecular shapes of TeF_4 and BrF_5 and indicate these deviations on your drawing.

***10.126** *The two electron pairs in a double bond repel other electron pairs more than the single pair of electrons in a single bond.* On the basis of this statement, which bond angles should be larger in SO_2Cl_2, the O—S—O bond angles or the Cl—S—Cl bond angles? In the molecule, sulfur is bonded to two oxygen atoms and two chlorine atoms. (*Hint*: Assign formal charges and work with the best Lewis structure for the molecule.)

10.127 In a certain molecule, a *p* orbital overlaps with a *d* orbital as shown at the right. The algebraic signs of the lobes of the *d*-orbital wave function are also indicated in the drawing. Which kind of bond is formed, σ or π? Explain your choice. Repeat the drawing twice on a separate sheet of paper. In one of them, indicate the signs of the lobes of the *p*-orbital wave function that would lead to a bonding MO. In the other, indicate the signs of the lobes of the *p*-orbital wave function that would lead to an antibonding MO.



10.128 If we assign the internuclear axis in a diatomic molecule to be the *z* axis, what kind of *p* orbital (p_x, p_y, or p_z) on one atom would have to overlap with a d_{xz} orbital on the other atom to give a pi bond?

Multi-Concept Problems

*10.129 The peroxynitrite ion, OONO⁻, is a potent toxin formed in cells affected by diseases such as diabetes and atherosclerosis. Peroxynitrite ion can oxidize and destroy biomolecules crucial for the survival of the cell.

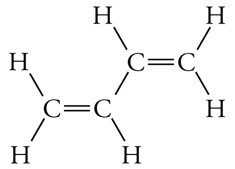
(a) Give the O—O—N and O—N—O bond angles in the peroxynitrite ion.

(b) What is the hybridization of the N atom in the peroxynitrite ion?

(c) Suggest why the peroxynitrite ion is expected to be much less stable than the nitrate ion, NO_3^-.

*10.130 An ammonia molecule, NH_3, is very polar, whereas NF_3 is almost nonpolar. Use this observation along with the valence bond description of bonding in these molecules to justify the following statement: *Lone pairs in hybrid orbitals contribute to the overall dipole moment of a molecule.*

*10.131 There exists a hydrocarbon called butadiene, which has the molecular formula C_4H_6 and the structure



The C═C bond lengths are 134 pm (about what is expected for a carbon–carbon double bond), but the C—C bond length in this molecule is 147 pm, which is shorter than a normal C—C single bond. The molecule is planar (i.e., all the atoms lie in the same plane).

(a) What kind of hybrid orbitals do the carbon atoms use in this molecule to form the C—C bonds?

(b) Between which pairs of carbon atoms do we expect to find sideways overlap of *p* orbitals (i.e., π-type *p-p* overlap)?

(c) Based on your answer to parts (a) and (b), explain why the center carbon–carbon bond is shorter than a carbon–carbon single bond.

*10.132 A 0.244 g sample of a compound of phosphorus and bromine, when dissolved in water, reacted to give a solution containing phosphorous acid and bromide ion. Addition of excess $AgNO_3$ solution to the mixture led to precipitation of AgBr. When the precipitate of AgBr was collected and dried, it weighed 0.508 g. Determine the chemical formula of the phosphorus–bromine compound and predict whether its molecules are polar or nonpolar.

Exercises in Critical Thinking

10.133 Five basic molecular shapes were described for simple molecular structures containing a central atom bonded to various numbers of surrounding atoms. Can you suggest additional possible structures? Provide arguments about the likelihood that these other structures might actually exist.

10.134 Compare and contrast the concepts of delocalization and resonance.

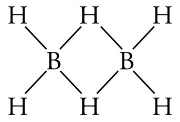
10.135 Why doesn't a carbon–carbon quadruple bond exist?

10.136 What might the structure of the iodine heptafluoride molecule be? If you can think of more than one possible structure, which is likely to be of lowest energy based on the VSEPR model?

10.137 The F—F bond in F_2 is weaker than the Cl—Cl bond in Cl_2. How might the lone pairs on the atoms in the molecules be responsible for this?

10.138 Molecular orbital theory predicts the existence of antibonding molecular orbitals. How do antibonding electrons affect the stability in a molecule?

10.139 The structure of the diborane molecule, B_2H_6, is sometimes drawn as



There are not enough valence electrons in the molecule to form eight single bonds, which is what the structure implies. Assuming that the boron atoms use sp^3 hybrid orbitals, suggest a way that hydrogen 1*s* orbitals can be involved in forming delocalized molecular orbitals that bridge the two boron atoms. Use diagrams to illustrate your answer. What would be the average bond order in the bridging bonds?

Chapters 8–10

Bringing It Together

Once again we pause to provide an opportunity for you to see how well you have grasped the concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–7. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. A beam of green light has a wavelength of 500 nm. What is the frequency of this light? What is the energy, in joules, of one photon of this light? What is the energy, in joules, of one mole of photons of this light? Would blue light have more or less energy per photon than this light?

2. Write the abbreviated electron configuration and construct the orbital diagram for the chromium(III) ion. Is the ion paramagnetic or diamagnetic?

3. Ozone, O_3, consists of a chain of three oxygen atoms.

(a) Draw the two resonance structures for ozone that obey the octet rule.

(b) Based on your answer to (a), is the molecule linear or nonlinear?

(c) Assign formal charges to the atoms in the resonance structures you have drawn in part (a).

(d) On the basis of your answers to (b) and (c), explain why ozone is a polar molecule even though it is composed of three atoms that have identical electronegativities.

4. Which of the following processes are endothermic?

(a) $P^-(g) + e^- \longrightarrow P^{2-}(g)$

(b) $Fe^{3+}(g) + e^- \longrightarrow Fe^{2+}(g)$

(c) $Cl(g) + e^- \longrightarrow Cl^-(g)$

(d) $S(g) + 2e^- \longrightarrow S^{2-}(g)$

5. For each of the following, select the particle that has the specified property.

(a) The atom with the larger radius: Rb or Sr

(b) The particle with the larger radius: Mn^{2+} or Mn^{3+}

(c) The atom with the larger radius: P or As

(d) The atom with the more endothermic ionization energy: O or F

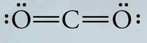
(e) The atom with the more endothermic ionization energy: Be or B

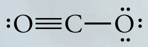
(f) The atom with the more exothermic electron affinity: O or S

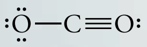
6. Give the electron configurations of the ions (a) Pb^{2+}, (b) Pb^{4+}, (c) S^{2-}, (d) Fe^{3+}, and (e) Zn^{2+}. Which of the ions are paramagnetic and which are diamagnetic?

7. Why is the change in atomic size, going from one element to the next across a period, smaller among the transition elements than among the representative elements?

8. Some resonance structures that can be drawn for carbon dioxide are shown below.


I

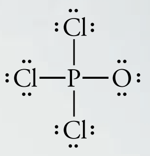

II

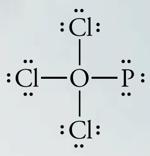

III

Explain why Structure I is the preferred structure.

9. Predict the shapes of the following molecules and ions: (a) SbH_3, (b) IF_3, (c) $HClO_2$, (d) C_2^{2-}, (e) AsF_5, (f) O_2^{2-}, (g) HCO_3^-, (h) TeF_6, (i) HNO_3.

10. Why, on the basis of formal charges and relative electronegativities, is it more reasonable to expect the structure of $POCl_3$ to be the one on the left rather than the one on the right?





Is either of these the "best" Lewis structure that can be drawn for this molecule?

11. The melting point of Al_2O_3 is much higher than the melting point of NaCl. On the basis of lattice energies, explain why this is so.

12. A certain element X was found to form three compounds with chlorine having the formulas XCl_2, XCl_4, and XCl_6. One of its oxides has the formula XO_3, and X reacts with sodium to form the compound Na_2X.

(a) Is X a metal or a nonmetal?

(b) In which group in the periodic table is X located?

(c) In which periods in the periodic table could X possibly be located?

(d) Draw Lewis structures for XCl_2, XCl_4, XCl_6, and XO_3. (Where possible, follow the octet rule.) Which has multiple bonding?

(e) What do we expect the molecular structures of XCl_2, XCl_4, XCl_6, and XO_3 to be? Which are polar molecules?

(f) The element X also forms the oxide XO_2. Draw a Lewis structure for XO_2 that obeys the octet rule.

(g) Assign formal charges to the atoms in the Lewis structures for XO_2 and XO_3 drawn for parts (d) and (f).

(h) What kinds of hybrid orbitals would X use for bonding in XCl_4 and XCl_6?

(i) If X were to form a compound with aluminum, what would be its formula?

(j) Which compound of X would have the more ionic bonds, Na_2X or MgX?

(k) If X were in Period 5, what would be the electron configuration of its valence shell?

13. Construct a Born–Haber cycle for the formation of RbBr from its elements that includes the lattice energy as an energy term along one of the paths from Rb(*s*) and $Br_2(l)$ to RbBr(*s*). Identify the various energy terms involved and indicate which are endothermic and which are exothermic.

14. The heat of formation of $CaCl_2$ is −795 kJ/mol. The energy needed to change one mole of Ca(*s*) into one mole of Ca(*g*) is +192 kJ/mol. The first and second ionization energies of Ca are +590 kJ/mol and +1146 kJ/mol, respectively. The bond energy of Cl_2 is 238 kJ per mole of Cl—Cl bonds. The electron affinity of Cl is −348 kJ/mol. Set up a Born–Haber cycle and calculate the lattice energy of $CaCl_2$. Report the lattice energy in units of kJ/mol.

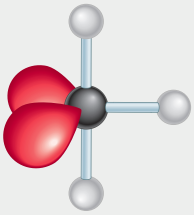
15. For each of the following pairs of compounds, which has the larger lattice energy: (a) MgO or NaCl, (b) MgO or BeO, (c) NaI or NaF, (d) MgO or CaS? Explain your choices.

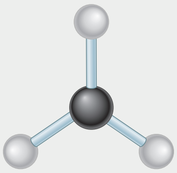
16. The oxalate ion has the following arrangement of atoms.

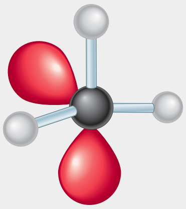
O O
C C
O O

Draw all of its resonance structures.

17. According to the VSEPR model, which of the following best illustrates the structure of the $AsCl_3{}^{2-}$ ion?


(a)


(b)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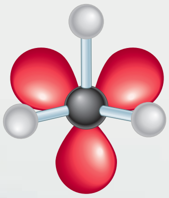
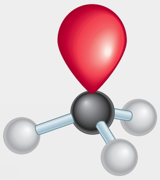
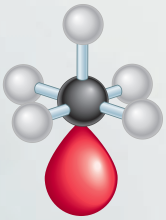
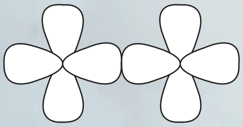

(d)

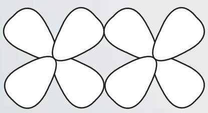

(e)

18. The VSEPR model predicts the structure below for a certain molecule. Which kind of hybrid orbitals does the central atom in the molecule use to form its covalent bonds?



19. Which kind of bond, σ or π, is produced by the overlap of *d* orbitals pictured below?

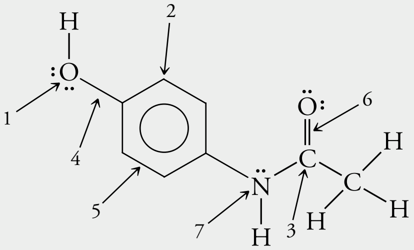
(a) 

(b) 

20. For the orbital interactions in the preceding problem, sketch the shapes you would expect for the bonding and antibonding orbitals created by the orbital overlap shown.

21. Which of the following molecules would be nonpolar: SbH_3, IF_3, AsF_5, $SbCl_3$, OF_2? Which has the most polar bonds?

22. The following is the chemical structure of acetaminophen, the pain killer in Tylenol®.



What kind of hybrid orbitals are used by atoms 1, 2, 3, and 7? How many sigma and pi bonds are in bonds 4 and 6? What is the average bond order in bond 5?

23. Construct the MO energy level diagram for the cyanide ion, keeping in mind that the more electronegative element has orbitals lower in energy than the less electronegative element. What is the bond order in this ion? Compare the valence bond and molecular orbital descriptions of bonding in this ion.

24. The simple hydrogen compound of arsenic is called arsine and has the formula AsH_3. The bond angles in the compound are 91.8°. Give a valence bond description of the bonding in this molecule that is consistent with the bond angles.

25. Predict the shapes of the following molecules and ions: (a) PF_3 (b) $PF_6{}^-$, (c) $PF_4{}^+$, and (d) PF_5. What kinds of hybrid orbitals does phosphorus use in each of them to form the bonds to fluorine atoms? Do any of these molecules contain what might be called a coordinate covalent bond?

26. Consider the following statements: (1) Fe^{2+} is easily oxidized to Fe^{3+}, and (2) Mn^{2+} is difficult to oxidize to Mn^{3+}. On the basis of the electron configurations of the ions, explain the difference in ease of oxidation.

27. The bond energy of O_2 is 501 kJ/mol. What is the wavelength of a photon needed to rupture the bond of a single oxygen molecule?

28. How would you expect the carbon–oxygen bond lengths to change relative to each other when an acetic acid molecule is neutralized by hydroxide ion?

11 Properties of Gases

Chapter Outline

11.1 | A Molecular Look at Gases
11.2 | Measurement of Pressure
11.3 | Gas Laws
11.4 | Stoichiometry Using Gas Volumes
11.5 | Ideal Gas Law
11.6 | Dalton's Law of Partial Pressures
11.7 | Kinetic Molecular Theory
11.8 | Real Gases
11.9 | Chemistry of the Atmosphere

Understanding the properties of gases saves lives. Molecular oxygen in the air is the essential gas that supports life and also combustion. Other gases, such as molecular nitrogen, will not support life nor fire, but, neither are they inherently toxic. However, many of the gases produced in the fire depicted here are toxic and need to be avoided as the firefighters in the accompanying photo are doing. While the fire department tells us what to do in a fire, this chapter will help us *understand why* we should do it. The properties of gases we study now also explain many other common phenomena we see and use in our daily lives. © Radius Images/Corbis

This Chapter in Context

In the preceding chapters we've discussed the chemical properties of a variety of different substances. We've also studied the kinds of forces (chemical bonds) that hold molecular and ionic substances together. In fact, it is the nature of the chemical bonds that dictates chemical properties. With this chapter we begin a systematic study of the *physical properties* of materials, including the factors that govern the behavior of gases, liquids, and solids. We study gases first because they are the easiest to understand and their behavior will help explain some of the properties of liquids and solids in Chapter 12.

We live in a mixture of gases called the earth's atmosphere. Through everyday experience, you have become familiar with many of the properties that gases have. Our goal in this chapter is to refine this understanding in terms of the physical laws that govern the way gases behave. You will also learn how this behavior is interpreted in terms of the way we view gases at a molecular level. In our discussions we will describe how the energy concepts, first introduced to you in Chapter 7, provide an explanation of the gas laws. Finally, you will learn how a close examination of gas properties furnishes clues about molecular size and the attractions that exist between molecules.

11.1 | A Molecular Look at Gases

To early observers the mass loss of a rotting apple or the mass gain of a rusting nail was inexplicable. For a long time, these early scientists didn't recognize the existence of gases as examples of matter and the answer to their perplexing observations. Of course, we now understand that gases are composed of chemical substances that exist in one of the three common states of matter. The reason for the early confusion is that the physical properties of gases differ so much from those of liquids and solids. Consider water, for example. We can see and feel it as a liquid, but it seems to disappear when it evaporates and surrounds us as water vapor. With this in mind, let's examine some of the properties of gaseous substances to look for clues that suggest the nature of gases when viewed at a molecular level.

Because air has so little weight for a given volume, it makes things filled with air float, much to the pleasure of these balloonists at a hot-air balloon festival. *(Raymond Watt/Albuquerque International Balloon Fiesta, Inc.)*

Familiar Properties of Gases

The most common gas, familiar to everyone, is air. Because you've grown up surrounded by this gas, you already are aware of many properties that gases have. Let's look at two of them.

- You can wave your hand through air with little resistance. (Compare that with waving your hand through a tub filled with water.)
- The air in a bottle has little weight to it, so if a bottle of air is submerged under water and released, it quickly bobs to the surface.

Both of these observations suggest that a given volume of air doesn't have much matter in it. (We can express this by saying that air has a low density.) What else do you know about gases?

■ Dry air is roughly 21% O_2 and 78% N_2, but it has traces of several other gases.

- Gases can be compressed. Inflating a tire involves pushing more and more air into the same container (the tire). This behavior is a lot different from that of liquids; you can't squeeze more water into an already filled bottle.
- Gases exert a pressure. Whenever you inflate a balloon you have an experience with gas pressure, and the "feel" of a balloon suggests that the pressure acts equally in all directions.

Suave
FREESIA
FLEXIBLE HOLD
HAIRSPRAY

Aerosol cans carry a warning about subjecting them to high temperatures because the internal pressure can become large enough to cause them to explode. *(Andy Washnik)*

- The pressure of a gas depends on *how much* gas is confined. The *more air* you pump into a tire, the greater the pressure.
- Gases fill completely any container into which they're placed—you've never heard of half a bottle of air. If you put air in a container, it expands and fills the container's entire volume. (This is certainly a lot different from the behavior of liquids and solids.)
- Gases mix freely and quickly with each other. You've experienced this when you've smelled the perfume of someone passing by. The vapors of the person's perfume mix with and spread through the air.
- The pressure of a gas rises when its temperature is increased. That's why there's the warning "Do Not Incinerate" printed on aerosol cans. A sealed can, if made too hot, is in danger of exploding from the increased pressure.

Molecular Model of Gases

The simple qualitative observations about gases described above suggest what gases must be like when viewed at the molecular level (Figure 11.1). The fact that there's so little matter in a given volume suggests that there is a lot of space between the individual molecules, especially when compared to liquids or solids. This would also explain why gases can be so easily compressed—squeezing a gas simply removes some of the empty space.

It also seems reasonable to believe that the molecules of a gas are moving around fairly rapidly. How else could we explain how molecules of a perfume move so quickly through the air? Furthermore, if gas molecules didn't move, gravity would cause them to settle to the bottom of a container (which they don't do). And if gas molecules are moving, some must be colliding with the walls of the container, and the force of these tiny collisions would explain the pressure a gas exerts. It also explains why adding more gas increases the pressure; the more gas in the container, the more collisions with the walls, and the higher the pressure.

Finally, the fact that gas pressure rises with increasing temperature suggests that the molecules move faster with increasing temperature, because faster molecules would exert greater forces when they collide with the walls.

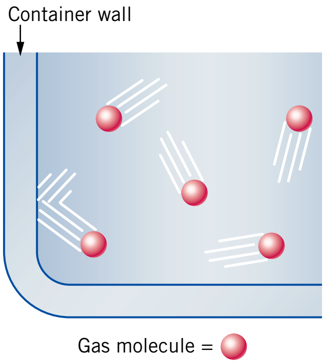


Figure 11.1 | **A gas viewed at the molecular level.** Simple qualitative observations of the properties of gases lead us to conclude that a gas is composed of widely spaced molecules that are in constant motion. Collisions of molecules with the walls produce tiny forces that, when taken all together, are responsible for the gas pressure.

11.2 | Measurement of Pressure

As we discussed in Chapter 7, **pressure** *is force per unit area*, calculated by dividing the force by the area over which the force acts.

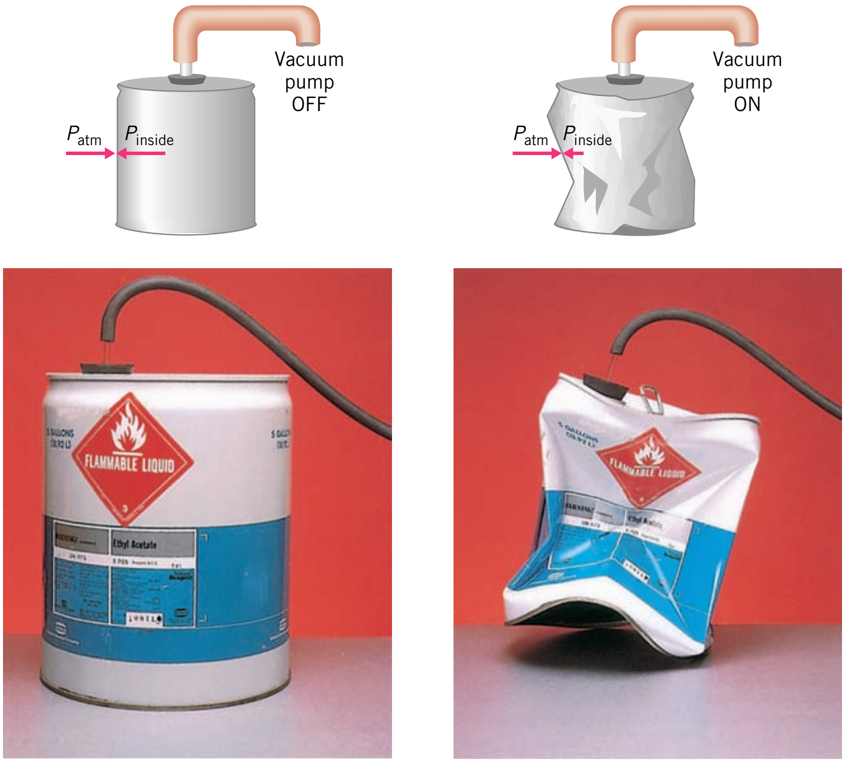
$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Earth exerts a gravitational force on everything with mass that is on it or near it. What we call the *weight* of an object, like this book, is simply our measure of the force it exerts because gravity acts on it.

The Barometer

Earth's gravity pulls on the air mass of the atmosphere, causing it to cover the Earth's surface like an invisible blanket. The molecules in the air collide with every object the air contacts, and by doing so, produce a pressure we call the *atmospheric pressure.*

At any particular location on Earth, the atmospheric pressure acts equally in all directions—up, down, and sideways. In fact, it presses against our bodies with a surprising amount of force, but we don't really feel it because the fluids in our bodies push back with equal pressure. We can observe atmospheric pressure, however, if we pump the air from



(*a*)

(*b*)

Figure 11.2 | **The effect of an unbalanced pressure.** (*a*) The pressure inside the can, P_{inside}, is the same as the atmospheric pressure outside, P_{atm}. The pressures are balanced; $P_{inside} = P_{atm}$. (*b*) When a vacuum pump reduces the pressure inside the can, P_{inside} becomes less than P_{atm}, and the unbalanced outside pressure quickly and violently makes the can collapse. *(OPC, Inc)*

a collapsible container such as the can in Figure 11.2. Before air is removed, the walls of the can experience atmospheric pressure equally inside and out. When some air is pumped out, however, the pressure inside decreases, making the atmospheric pressure outside of the can greater than the pressure inside. The net inward pressure is sufficiently great to make the can crumple.

To measure atmospheric pressure we use a device called a **barometer**. The simplest type is the *Torricelli barometer*[1] (Figure 11.3), which consists of a glass tube sealed at one end, 80 cm or more in length. To set up the apparatus, the tube is filled with mercury, capped, inverted, and then its capped end is immersed in a dish of mercury. When the cap is removed, some, but not all, of the mercury runs out.[2] When, due to its pressure, mercury flows from the tube, the level of the mercury in the dish must rise. Atmospheric pressure, pushing on the surface of the mercury in the dish, opposes this rise in mercury level. Rapidly, the two pressures become equal, and no more mercury can run out. However, a space inside the tube above the mercury level has been created having essentially no atmosphere; it's a *vacuum.*

The height of the mercury column, measured from the surface of the mercury in the dish, is directly proportional to atmospheric pressure. On days when the atmospheric pressure is high, more mercury is forced from the dish into the tube and the height of the column increases. When the atmospheric pressure drops—during an approaching storm, for example—some mercury flows out of the tube and the height of the column decreases. Most people live where this height fluctuates between 730 and 760 mm.

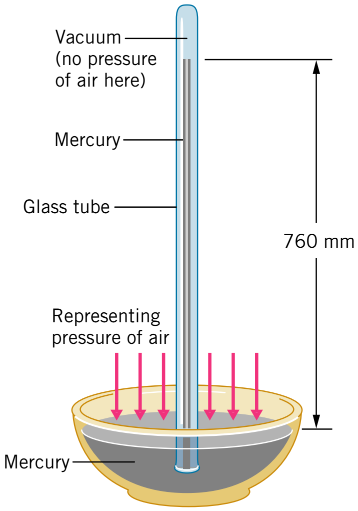


Figure 11.3 | **A Torricelli barometer.** The apparatus is also called a mercury barometer. The height of the mercury column inside the tube is directly proportional to the atmospheric pressure. In the United States, weather reports often give the height of the mercury column in inches.

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[1] In 1643 Evangelista Torricelli, an Italian mathematician, suggested an experiment, later performed by a colleague, that demonstrated that atmospheric pressure determines the height to which a fluid will rise in a tube inverted over the same liquid. This concept led to the development of the Torricelli barometer, which is named in his honor.

[2] Today, mercury is kept as much as possible in closed containers. Although atoms of mercury do not readily escape into the gaseous state, mercury vapor is a dangerous poison.

Units of Pressure

■ In English units, one atmosphere of pressure is 14.7 lb/in^2. This means that at sea level, each square inch of your body is experiencing a force of nearly 15 pounds.

At sea level, the height of the mercury column in a barometer fluctuates around a value of 760 mm. Some days it's a little higher, some a little lower, depending on the weather. The average pressure at sea level has long been used by scientists as a standard unit of pressure. The **standard atmosphere (atm)** was originally defined as the pressure needed to support a column of mercury 760 mm high measured at 0 °C.[3]

In the SI, the unit of pressure is the **pascal**, symbolized **Pa**. In SI units, the pascal is the ratio of force in *newtons* (N, the SI unit of force) to area in meters squared,

$$1\text{ Pa} = \frac{1\text{ N}}{1\text{ m}^2} = 1\text{ N m}^{-2}$$

It's a very small pressure; 1 Pa is approximately the pressure exerted by the weight of a lemon spread over an area of 1 m^2.

To bring the standard atmosphere unit in line with other SI units, it has been redefined in terms of the pascal as follows.

$$1\text{ atm} = 101{,}325\text{ Pa (exactly)}$$

A satellite photo of Hurricane Wilma when it reached Category 5 strength, with sustained winds of 175 miles per hour in the eye wall. *(Terra MODIS data acquired by direct broadcast at the University of South Florida; Judd Taylor. Image processed at the University of Wisconsin-Madison)*

A unit of pressure related to the pascal is the **bar**, which is defined as 100 kPa. Consequently, one bar is slightly smaller than one standard atmosphere (1 bar = 0.9868 atm). You may have heard the **millibar** unit (1 mb = 10^{-3} bar) used in weather reports describing pressures inside storms such as hurricanes. For example, the lowest atmospheric pressure at sea level ever observed in the Atlantic basin was 882 mb during Hurricane Wilma on October 19, 2005. The storm later weakened but still caused extensive damage as it crossed Florida.

For ordinary laboratory work, the pascal (or kilopascal) is not a conveniently measured unit. Usually we use a unit of pressure called the **torr** (named after Torricelli). The torr is defined as 1/760th of 1 atm.

$$1\text{ torr} = \frac{1}{760}\text{ atm}$$
$$1\text{ atm} = 760\text{ torr (exactly)}$$

The torr is very close to the pressure that is able to support a column of mercury 1 mm high. In fact, the *millimeter of mercury* (abbreviated *mm Hg*) is often itself used as a pressure unit. Except when the most exacting measurements are being made, it is safe to use the relationship

$$1\text{ torr} = 1\text{ mm Hg}$$

Below are values of the standard atmosphere (atm) expressed in different pressure units. Studying the table will give you a feel for the sizes of the different units.

760 torr
101,325 Pa
101.325 kPa
1.013 bar
1013 mb
14.7 lb in.$^{-2}$
1.034 kg cm^{-2}

---

[3] Because any metal, including mercury, expands or contracts as the temperature increases or decreases, the height of the mercury column varies with temperature (just as in a thermometer). Therefore, the definition of the standard atmosphere required that the temperature at which the mercury height is measured be specified.

Practice Exercises

11.1 | Using the table on page 476 determine the atmospheric pressure in pounds per square inch and inches of mercury when the barometer reads 730 mm Hg. (*Hint:* Recall your tools for converting units.)

11.2 | The second lowest barometric pressure ever recorded at sea level in the Western Hemisphere was 888 mb during Hurricane Gilbert in 1988. What was the pressure in pascals and torr?

Manometers

Gases used as reactants or formed as products in chemical reactions are kept from escaping by using closed glassware. To measure pressures inside such vessels, a **manometer** is used. Two types are common: open-end and closed-end manometers.

Open-End Manometers

An **open-end manometer** consists of a U-tube partly filled with a liquid, usually mercury (see Figure 11.4). One arm of the U-tube is open to the atmosphere; the other is exposed to a container of some trapped gas. In part (*a*) of this diagram, the mercury levels are equal and the pressure inside the flask is equal to the atmospheric pressure. The second part of the figure, 11.4*b*, shows the mercury level as being higher in the arm exposed to the atmosphere. We conclude that the pressure in the flask is greater than atmospheric pressure. In Figure 11.4*c*, the Hg is higher in the arm connected to the container of gas, indicating that the pressure of the atmosphere must be *higher* than the gas pressure. With mercury in the tube, the difference in the heights in the two arms, represented here as P_{Hg}, is equal to the difference between the pressure of the gas and the pressure of the atmosphere. By measuring P_{Hg} in millimeters, the value equals the pressure difference in torr. For the situation shown in Figure 11.4*b*, we would calculate the pressure of the trapped gas as

■ Advantages of mercury over other liquids are its low reactivity, its low melting point, and particularly its very high density, which permits short manometer tubes.

$$P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}} \quad (\text{when } P_{\text{gas}} > P_{\text{atm}})$$

In Figure 11.4*c* the calculation of the pressure is

$$P_{\text{gas}} = P_{\text{atm}} - P_{\text{Hg}} \quad (\text{when } P_{\text{gas}} < P_{\text{atm}})$$

Example 11.1 illustrates how the open-end manometer is used.

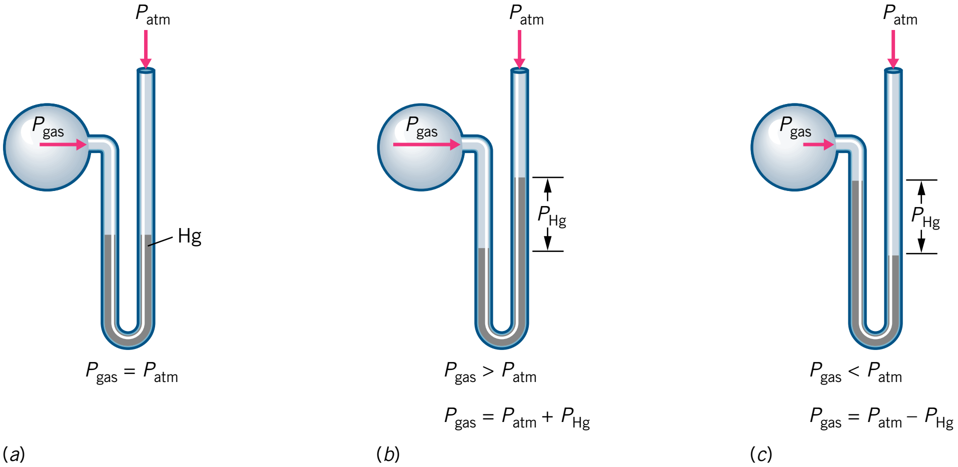
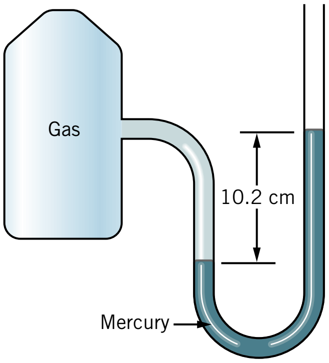

P_{atm}
P_{gas}
Hg
$P_{\text{gas}} = P_{\text{atm}}$
(*a*)
P_{atm}
P_{gas}
P_{Hg}
$P_{\text{gas}} > P_{\text{atm}}$
$P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}}$
(*b*)
P_{atm}
P_{gas}
P_{Hg}
$P_{\text{gas}} < P_{\text{atm}}$
$P_{\text{gas}} = P_{\text{atm}} - P_{\text{Hg}}$
(*c*)

Figure 11.4 | **An open-end manometer.** The difference in the heights of the mercury in the two arms equals the pressure difference, in torr, between the atmospheric pressure, P_{atm}, and the pressure of the trapped gas, P_{gas}.

Example 11.1

Measuring the Pressure of a Gas Using a Manometer



A student collected a gas in an apparatus connected to an open-end manometer, as illustrated in the figure in the margin. The difference in the heights of the mercury in the two columns was 10.2 cm and the atmospheric pressure was measured to be 756 torr. What was the pressure of the gas in the apparatus?

■ **Analysis:** From the preceding discussion, we know that when using an open-end manometer we will use the atmospheric pressure and either add to it or subtract from it—but which should we do? In a problem of this type, it is best to use some common sense (something that will help a lot in working problems involving gases).

When we look at the diagram of the apparatus, we see that the mercury is pushed up into the arm of the manometer that's open to the air. Common sense tells us that the pressure of the gas inside must be larger than the pressure of the air outside. Therefore, we will add the pressure difference to the atmospheric pressure.

Finally, before we can do the arithmetic, we must be sure the pressure difference is calculated in torr.

■ **Assembling the Tools:** We need the equation for determining the pressure in an open-end manometer,

$$P_{\text{gas}} = P_{\text{atm}} \pm P_{\text{Hg}}$$

where we add or subtract P_{Hg} depending on which side of the manometer has the higher mercury level. We use the usual conversion factors for SI prefixes from Table 2.4 on page 35 to perform the conversion needed.

$$10^{-2}\ \text{m} = 1\ \text{cm} \quad \text{and} \quad 10^{-3}\ \text{m} = 1\ \text{mm}$$

The other conversion we need is the equality between 1 mm Hg and 1 torr.

■ **Solution:** We first need to convert cm Hg to mm Hg, so we use our conversion factors to write

$$10.2\ \cancel{\text{cm}}\ \text{Hg} \times \frac{10^{-2}\ \cancel{\text{m}}}{1\ \cancel{\text{cm}}} \times \frac{1\ \text{mm}}{10^{-3}\ \cancel{\text{m}}} = 102\ \text{mm Hg} = 102\ \text{torr}$$

$$102\ \text{mm Hg} = 102\ \text{torr}$$

Based on our analysis, to find the gas pressure, we add 102 torr to the atmospheric pressure.

$$\begin{aligned} P_{\text{gas}} &= P_{\text{atm}} + P_{\text{Hg}} \\ &= 756\ \text{torr} + 102\ \text{torr} \\ &= 858\ \text{torr} \end{aligned}$$

The gas pressure is 858 torr.

■ **Is the Answer Reasonable?** We can check our conversions because the number of mm should always be larger than the measurement expressed in cm. We can also double-check that we've done the right *kind* of arithmetic (i.e., adding or subtracting). Look at the apparatus again. If the gas pressure were lower than atmospheric pressure, it would appear as though the atmosphere was pushing the mercury higher on the apparatus side of the manometer in the same way that the heavier child on a see-saw pushes his lighter friend higher. That's not what we see here. It almost looks like the gas is trying to push the mercury out of the manometer, so we conclude that the gas pressure must be higher than atmospheric pressure. That's exactly what we've found in our calculation, so we can feel confident we've solved the problem correctly.

Practice Exercises

11.3 | An open-end manometer is filled with mercury so that each side has a height equal to 25 cm. If the atmospheric pressure is 770 torr on a given day, what are the approximate maximum and minimum pressures that this manometer can measure? (*Hint:* What is the maximum difference in mercury height for this manometer?)

11.4 | In another experiment that same day, it was found that the mercury level in the arm of the manometer attached to the container of gas was 11.7 cm higher than in the arm open to the air. What was the pressure of the gas?

Closed-End Manometers

A **closed-end manometer** (Figure 11.5) is made by sealing the arm that will be farthest from the gas sample and then filling the closed arm completely with mercury. When the gas pressures to be measured are expected to be small, the filled arm can be made short, making the entire apparatus compact. In this design, the mercury is pushed to the top of the closed arm when the open arm of the manometer is exposed to the atmosphere. When connected to a gas at a low pressure, however, the mercury level in the sealed arm will drop, leaving a vacuum above it. The pressure of the gas can then be measured just by reading the difference in heights of the mercury in the two arms, P_{Hg}. No separate measurement of the atmospheric pressure is required.

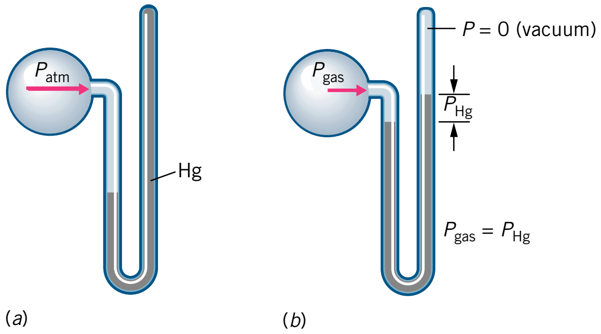


Figure 11.5 | **A closed-end manometer for measuring gas pressures less than 1 atm or 760 torr.** (*a*) When constructed, the tube is fully evacuated and then mercury is allowed to enter the tube to completely fill the closed arm. (*b*) When the tube is connected to a bulb containing a gas at low pressure, the difference in the mercury heights (P_{Hg}) equals the pressure, in torr, of the trapped gas P_{gas}.

Manometers with Liquids Other than Mercury

Scientists often use manometers with liquids other than mercury. One compelling reason is to reduce the possibility of a hazardous mercury spill. Another reason is that more precise measurements may be made using other liquids and then converting to the equivalent in mercury. Water, ethyl alcohol, mineral oil, and many other liquids may be used in place of mercury.

In order to convert the difference in heights of a liquid to the equivalent height in mercury, we need to know the density of the substitute liquid. We can reason that the height of different liquids, measuring the same pressure, should be inversely proportional to their densities.

$$\frac{\text{height liquid 1}}{\text{height liquid 2}} = \frac{\text{density liquid 2}}{\text{density liquid 1}}$$

If liquid 1 is mercury, we can rearrange the equation to read

$$\text{mm Hg} = \text{mm liquid} \times \frac{\text{density of liquid}}{\text{density Hg}}$$

This will allow us to use any liquid with a known density in a manometer and then convert the readings to the equivalent in mm Hg.

■ Ten meters is about 33 feet or the height of a three-story building.

Let's consider what will happen if we use water instead of mercury in a manometer. Because of the low density of water compared to the high density of mercury, we will observe a height of water that is 13.6 times the height of mercury. The practical result of using a water manometer is that measurements will be 13.6 times more precise than those using a mercury manometer. The drawback is that a water manometer used to measure barometric pressure would have to be more than 10 meters high.

Modern Pressure Sensors

Digital tire gauge. *(David J. Green/Alamy)*

Membrane pressure sensor with blue-colored membrane exposed. *(Photo courtesy of Pressure Systems)*

Manometers are obvious in the way readings are related to gas pressures. However, there are a large number of different, and often more convenient, devices in use today.

Almost everyone is familiar with a tire gauge to make sure the pressure in a car tire is correct. The mechanical version is based on the pressure in the tire pushing against a plunger (with the scale on it) attached to a spring. When the force exerted by the tire pressure and the force of the compressed spring are equal, the plunger stops moving and the pressure can be read from the scale. Another device, called a Bourdon tube, relies on gas pressure expanding a coil of tubing. As the coil expands it rotates. A pointer and calibrated scale are attached to measure this rotation as a pressure reading.

Automatic electronic pressure sensors, such as the digital tire pressure gauge, are based on electrical or mechanical properties of thin metallic or plastic membranes that change when pressure is applied. These properties can be monitored continuously, and this type of pressure-measuring device is useful for remote sensors such as deep-sea measurements.

Measurement of very low pressures uses specialized equipment. One device, called an ionization gauge, measures the number of ions that can be produced at charged electrodes. The lower the pressure, the fewer the number of ions produced. Pressures from 10^{-2} to 10^{-11} torr can be measured; however, the gauge must be calibrated because the type of gas molecule present affects the number of ions produced.

11.3 | Gas Laws

Earlier, we examined some properties of gases that are familiar to you. Our discussion was only qualitative, however, and now that we've discussed pressure and its units, we are ready to examine gas behavior quantitatively.

There are four variables that affect the properties of a gas—pressure, volume, temperature, and the amount of gas. In this section, we will study situations in which the amount of gas (measured either by grams or moles) remains constant and observe how gas samples respond to changes in pressure, volume, and temperature.

Pressure–Volume Law

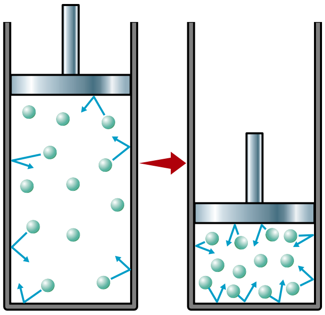


Figure 11.6 | **Compressing a gas increases its pressure.** A molecular view of what happens when a gas is squeezed into a smaller volume. By crowding the molecules together, the number of collisions with a given area of the walls increases, which causes the pressure to rise.

When you inflate a bicycle tire with a hand pump, you squeeze air into a smaller volume and increase its pressure. Packing molecules into a smaller space causes an increased number of collisions with the walls, and because these collisions are responsible for the pressure, the pressure increases (Figure 11.6).

Robert Boyle, an Irish scientist (1627–1691), performed experiments to determine quantitatively how the volume of a fixed amount of gas varies with pressure. Because the volume is also affected by the temperature, he held that variable constant. A graph of typical data collected in his experiments is shown in Figure 11.7*a* and demonstrates that *the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure.* Mathematically, this can be expressed as

$$V \propto \frac{1}{P} \qquad \text{(temperature and amount of gas held constant)}$$

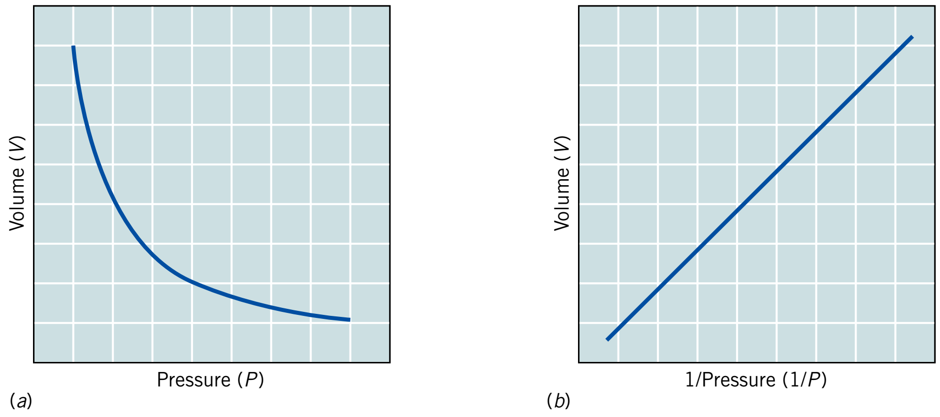


Figure 11.7 | **The variation of volume with pressure at constant temperature for a fixed amount of gas.** (*a*) A typical graph of volume versus pressure, showing that as the pressure increases, the volume decreases. (*b*) A straight line is obtained when volume is plotted against $1/P$, which shows that $V \propto 1/P$.

where V is the volume and P is the pressure. This relationship between pressure and volume is now called **Boyle's law** or the **pressure–volume law**.

In the expression above, the proportionality sign, $\propto$, can be removed by introducing a proportionality constant, C.

$$V = \frac{1}{P} \times C$$

Rearranging gives

$$PV = C$$

This equation tells us, for example, that if at constant temperature the gas pressure is doubled, the gas volume must be cut in half so that the product of $P \times V$ doesn't change.

What is remarkable about Boyle's discovery is that *this relationship is essentially the same for all gases at temperatures and pressures usually found in the laboratory.*

Ideal Gases

When very precise measurements are made, it's found that Boyle's law doesn't quite work. This is especially a problem when the pressure of the gas is very high or when the gas is at a low temperature where it's on the verge of changing to a liquid. Although real gases do not *exactly* obey Boyle's law or any of the other gas laws that we'll study, it is often useful to imagine a hypothetical gas that would. We call such a hypothetical gas an *ideal gas*. An **ideal gas** *would obey the gas laws exactly over all temperatures and pressures.* A real gas behaves more and more like an ideal gas as its pressure decreases and its temperature increases. Most gases we work with in the lab can be treated as ideal gases unless we're dealing with extremely precise measurements.

Temperature–Volume Law

In 1787 a French chemist and mathematician named Jacques Alexander Charles became interested in hot-air ballooning, which at the time was becoming popular in France. His new interest led him to study what happens to the volume of a sample of gas when the temperature is varied, keeping the pressure constant.

■ Jacques Alexandre César Charles (1746–1823), a French scientist, had a keen interest in hot-air balloons. He was the first to inflate a balloon with hydrogen.

When data from experiments such as his are plotted, a graph like that shown in Figure 11.8 is obtained. Here the volume of the gas is plotted against the temperature in degrees Celsius. The colored points correspond to typical data, and the lines are drawn to most closely fit the data. Each line represents data collected for a different sample. Because all gases eventually become liquids if cooled sufficiently, the solid portions of the lines correspond to temperatures at which measurements are possible; at lower temperatures the

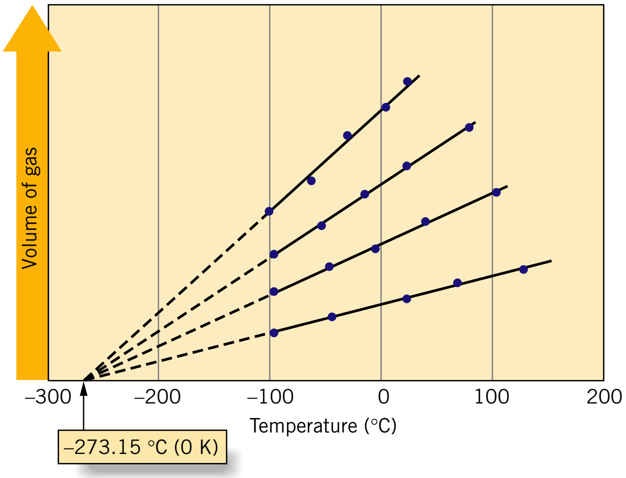


Figure 11.8 | **Charles' law plots.** Each line shows how the gas volume changes with temperature for a different-size sample of the same gas.

gas liquefies. However, if the lines are extrapolated (i.e., reasonably extended) back to a point where the volume of the gas would become zero if it didn't condense, all the lines meet at the same temperature, −273.15 °C. Especially significant is the fact that this exact same behavior is exhibited by all gases; when plots of volume versus temperature are extrapolated to zero volume, the temperature axis is always crossed at −273.15 °C. This point represents the temperature at which all gases, if they did not condense, would have a volume of zero, and below which they would have a negative volume. Negative volumes are impossible, of course, so it was reasoned that −273.15 °C must be nature's coldest temperature, and it was called **absolute zero.**

As you learned earlier, absolute zero corresponds to the zero point on the Kelvin temperature scale, and to obtain a Kelvin temperature, we add 273.15 °C to the Celsius temperature.[4]

$$T_K = t_C + 273.15$$

For most purposes, we will need only three significant figures, so we can use the following approximate relationship.

$$T_K = t_C + 273$$

The straight lines in Figure 11.8 suggest that at constant pressure, the volume of a gas is directly proportional to its temperature, provided the temperature is expressed in kelvins. This became known as **Charles' law** (or the **temperature–volume law)** and is expressed mathematically as

$$V \propto T \qquad \text{(pressure and amount of gas held constant)}$$

■ The value of C' depends on the size and pressure of the gas sample.

Using a different proportionality constant, C', we can write

$$V = C'T \qquad \text{(pressure and amount of gas held constant)}$$

Pressure–Temperature Law

■ Joseph Louis Gay-Lussac (1778–1850), a French scientist, was a co-discoverer of the element boron.

The French scientist Joseph Louis Gay-Lussac studied how the pressure and temperature of a fixed amount of gas at constant volume are related. (Such conditions exist, for example, when a gas is confined in a vessel with rigid walls, like an aerosol can.) The relationship that he established, called **Gay-Lussac's law** or the **pressure–temperature law**, states that *the pressure of a fixed amount of gas held at constant volume is directly proportional to the Kelvin temperature.* Thus,

$$P \propto T \qquad \text{(volume and amount of gas held constant)}$$

■ We're using different symbols for the various gas law constants because they are different for each law.

Using still another constant of proportionality, Gay-Lussac's law becomes

$$P = C''T \qquad \text{(volume and amount of gas held constant)}$$

Combined Gas Law

The three gas laws we've just examined can be brought together into a single equation known as the **combined gas law**, which states that *the ratio PV/T is a constant for a fixed amount of gas.*

$$\frac{PV}{T} = \text{constant} \qquad \text{(for a fixed amount of gas)}$$

---

[4] In Chapter 1 we presented this equation as $T_K = (t_C + 273.15\text{ °C})\left(\frac{1\text{ K}}{1\text{ °C}}\right)$ to emphasize unit cancellation. Operationally, however, we just add 273.15 to the Celsius temperature to obtain the Kelvin temperature (or we just add 273 if three significant figures are sufficient).

Usually, we use the combined gas law in problems where we know some given set of conditions of temperature, pressure, and volume (for a fixed amount of gas), and wish to find out how one of these variables will change when the others are changed. If we label the initial conditions of P, V, and T with the subscript 1 and the final conditions with the subscript 2, the combined gas law can be written in the following useful form.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{11.1}$$

TOOLS Combined gas law

In applying this equation, T must always be in kelvins. The pressure and volume can have any units, but whatever the units are on one side of the equation, they must be the same on the other side.

It is simple to show that Equation 11.1 contains each of the other gas laws as special cases. Boyle's law, for example, applies when the temperature is constant. Under these conditions, T_1 equals T_2 and the temperature cancels from the equation. This leaves us with

$$P_1V_1 = P_2V_2 \qquad \text{(when } T_1 \text{ equals } T_2\text{)}$$

which is one way to write Boyle's law. Similarly, under conditions of constant pressure, P_1 equals P_2 and the pressure cancels, so Equation 11.1 reduces to

$$V_1/T_1 = V_2/T_2 \qquad \text{(when } P_1 \text{ equals } P_2\text{)}$$

This, of course, is another way of writing Charles' law. Under the constant volume conditions required by Gay-Lussac's law, V_1 equals V_2, and Equation 11.1 reduces to

$$P_1/T_1 = P_2/T_2 \qquad \text{(when } V_1 \text{ equals } V_2\text{)}$$

CHEMISTRY OUTSIDE THE CLASSROOM | 11.1

Whipped Cream

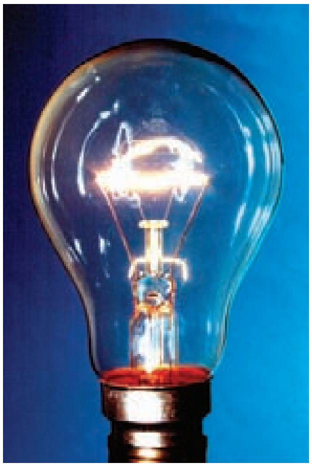
The dessert in Figure 1 looks tempting, but up until 1934 everyone had to whip their own cream by hand. Food scientists at the time were in the midst of using chemistry to produce a wide array of "convenience foods," foods that needed little or no preparation or cooking time.

Many foods can be canned—just look at the rows of vegetables, meats, and fruits lined up in the supermarket. Not only are these handy, but they also have exceptional shelf life compared to fresh vegetables, meats, and fruits. Fresh foods could be kept longer in refrigerators, which became commonly available in the 1930s. Freezers for frozen foods and ice cream came shortly thereafter. Now the consumer could have ice cream at home, but that wonderful sundae still needed the whipped cream.

Around 1934, Charles Getz was a graduate student in chemistry at the University of Illinois when he developed and sought a patent for producing a fluffy aerosol of gas bubbles entrained in cream. The concept was simple. Put some cream in a can, pressurize it with a gas, and when the gas is released along with the cream, it should foam up into whipped cream. Hundreds of gases were tried as propellants and they were all failures. Getz found that carbon dioxide did create a foam with milk, but it also gave the food a bad taste because of the sour taste of the acidic CO_2. He switched to nitrous oxide because it had no taste and provided a good product. It is now believed that the nonpolar CO_2 and N_2O work by dissolving in the nonpolar fats in liquid cream. When the pressure is released the gas expands to form tiny, relatively uniform bubbles to whip the cream. In 1935 Charles Getz applied for a process patent for his method of preparing whipped cream with nitrous oxide. He was issued Patent 2,294,172 in 1942. Aaron "Bunny" Lapin, an inventor from St. Louis, created Reddi-wip® real whipped cream in 1948.

Figure 1 Whipped cream dispensed from an aerosol container. *Envision/© Corbis*

Example 11.2
Using the Combined Gas Law



© *Tony Lilley Ci/Alamy*

An ordinary incandescent light bulb contains a tungsten filament, which becomes white hot (about 2500 °C) when electricity is passed through it. To prevent the filament from rapidly oxidizing, the bulb is filled to a low pressure with the inert (unreactive) gas argon. Suppose a 12.0 L cylinder containing compressed argon at a pressure of 57.8 atm measured at 24 °C is to be used to fill electric light bulbs, each with a volume of 158 mL, to a pressure of 3.00 torr at 21 °C. How many of these light bulbs could be filled by the argon in the cylinder?

Analysis: What do we need to know to figure out how many light bulbs can be filled? If we knew the total volume of gas with a pressure of 3.00 torr at 21 °C, we could just divide by the volume of one light bulb; the result is the number of light bulbs that can be filled. So our main problem is determining what volume the argon in the cylinder will occupy when its pressure is reduced to 3.00 torr and its temperature is lowered to 21 °C.

Assembling the Tools: Because the total amount of argon isn't changing, we can use the combined gas law for the calculation.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Solution: First, we will also make sure that the temperature is expressed in kelvins and that the values for P and V have the same units so that they cancel. To do this we need to convert 57.8 atm to torr,

$$57.8\ \cancel{\text{atm}} \times \frac{760\ \text{torr}}{1\ \cancel{\text{atm}}} = 4.39 \times 10^4\ \text{torr}$$

To use the combined gas law, let's construct a table of data being sure to assign the proper values to either the initial or final conditions.

	Initial (1)		Final (2)
P_1	4.39×10^4 torr	P_2	3.00 torr
V_1	12.0 L	V_2	?
T_1	297 K (24 + 273)	T_2	294 K (21 + 273)

To obtain the final volume, we solve for V_2. To do this we'll rearrange the equation so that V_2 is on one side of the equals sign and the remaining variables are on the other side.

$$V_2 = V_1 \times \underbrace{\frac{P_1}{P_2}}_{\text{Ratio of pressures}} \times \overbrace{\frac{T_2}{T_1}}^{\text{Ratio of temperatures}}$$

Notice that for V_2 to have the same units as V_1, the units in the numerator and denominator of both ratios must cancel. That's the reason we had to convert atmospheres to torr for P_1. Let's now substitute values from our table of data.

$$\begin{aligned} V_2 &= 12.0\ \text{L} \times \frac{4.39 \times 10^4\ \cancel{\text{torr}}}{3.00\ \cancel{\text{torr}}} \times \frac{294\ \cancel{\text{K}}}{297\ \cancel{\text{K}}} \\ &= 1.74 \times 10^5\ \text{L} \end{aligned}$$

Before we can divide by the volume of one light bulb (158 mL), we have to convert the total volume to milliliters.

$$1.74 \times 10^5 \ \cancel{\text{L}} \times \frac{1000 \text{ mL}}{1 \ \cancel{\text{L}}} = 1.74 \times 10^8 \text{ mL}$$

The volume per light bulb gives us the relationship

$$1 \text{ light bulb} \Leftrightarrow 158 \text{ mL argon}$$

which we can use to construct a conversion factor to find the number of light bulbs that can be filled.

$$1.74 \times 10^8 \ \cancel{\text{mL argon}} \times \frac{1 \text{ light bulb}}{158 \ \cancel{\text{mL argon}}} = 1.10 \times 10^6 \text{ light bulbs}$$

That's 1.10 million light bulbs! As you can see, there's not much argon in each one.

■ **Is the Answer Reasonable?** To determine whether we've set up the combined gas law properly, we check to see if the pressure and temperature ratios move the volume in the correct direction. Going from the initial to final conditions, the pressure *decreases* from 4.39×10^4 torr to 3.00 torr, so the volume should *increase* a lot. The pressure ratio we used is much larger than 1, so multiplying by it should increase the volume, which agrees with what we expect. Next, look at the temperature change; a *drop in temperature* should tend to *decrease* the volume, so we should be multiplying by a ratio that's less than 1. The ratio 293/298 is less than 1, so that ratio is correct, too.

■ Notice that we use our knowledge of how gases behave to determine whether we've done the correct arithmetic. If you learn to do this, you can catch your mistakes.

Now that our setup is okay, we check the math by rounding our numbers. One way we can round the numbers to estimate the answer is:

$$V_2 = 12.0 \text{ L} \times \frac{4.5 \times 10^4 \ \cancel{\text{torr}}}{3 \ \cancel{\text{torr}}} \times \frac{300 \ \cancel{\text{K}}}{300 \ \cancel{\text{K}}}$$

The estimated answer for $V_2 = 18 \times 10^4$ L, which is very close to our calculator answer. We can multiply the liters by 10^3 to get 18×10^7 mL and then we will "round" the 158 mL/bulb to 18×10^1 mL/bulb. Dividing the two gives us 1×10^6 bulbs. This again agrees quite well with the calculated answer.

(An observant student might note that in the end 12 L of argon must remain in the cylinder. However, we can divide 12,000 mL by 158 to get an answer of approximately 75 bulbs. Subtracting 75 from 1.09×10^6 still leaves us with 1.09×10^6 light bulbs.)

Practice Exercises

11.5 | Use the combined gas law to determine by what factor the pressure of an ideal gas must change if the Kelvin temperature is doubled and the volume is tripled. (*Hint:* Sometimes it is easier to assume a starting set of temperature, volume, and pressure readings and then apply the conditions of the problem.)

11.6 | A sample of nitrogen has a volume of 880 mL and a pressure of 740 torr. What pressure will change the volume to 870 mL at the same temperature?

11.7 | What will be the final pressure of a sample of nitrogen with a volume of 950 m^3 at 745 torr and 25.0 °C if it is heated to 60.0 °C and given a final volume of 1150 m^3?

11.4 | Stoichiometry Using Gas Volumes

Reactions at Constant *T* and *P*

When scientists studied reactions between gases quantitatively, they made an interesting discovery. If the volumes of the reacting gases, as well as the volumes of gaseous products, are measured under the same conditions of temperature and pressure, the volumes are in simple whole-number ratios. For example, hydrogen gas reacts with chlorine gas to give gaseous hydrogen chloride. Beneath the names in the following equation are the relative volumes with which these gases interact (at the same *T* and *P*).

$$\underset{\text{1 volume}}{\text{hydrogen}} + \underset{\text{1 volume}}{\text{chlorine}} \longrightarrow \underset{\text{2 volumes}}{\text{hydrogen chloride}}$$

What this means is that if we were to use 1.0 L of hydrogen, it would react with 1.0 L of chlorine and produce 2.0 L of hydrogen chloride. If we were to use 10.0 L of hydrogen, all the other volumes would be multiplied by 10 as well.

Similar simple, whole-number ratios by volume are observed when hydrogen combines with oxygen to give water, which is a gas above 100 °C.

$$\underset{\text{2 volumes}}{\text{hydrogen}} + \underset{\text{1 volume}}{\text{oxygen}} \longrightarrow \underset{\text{2 volumes}}{\text{water (gaseous)}}$$

Notice that the reacting volumes, *measured under identical temperatures and pressures*, are in ratios of simple, whole numbers.[5]

Observations such as those above led Gay-Lussac to formulate his **law of combining volumes**, which states that *when gases react at the same temperature and pressure, their combining volumes are in ratios of simple whole numbers*. Much later, it was learned that these "simple whole numbers" are the coefficients of the equations for the reactions.

Avogadro's Principle

■ Amedeo Avogadro (1776–1856), an Italian scientist, helped to put chemistry on a quantitative basis.

The observation that the gases react in whole-number volume ratios led Amedeo Avogadro to conclude that, at the same *T* and *P*, equal volumes of gases must have identical numbers of molecules. Today, we know that "equal numbers of *molecules*" is the same as "equal numbers of *moles*," so Avogadro's insight, now called **Avogadro's principle**, is expressed as follows: *When measured at the same temperature and pressure, equal volumes of gases contain equal numbers of moles.* A corollary to Avogadro's principle is that *the volume of a gas is directly proportional to its number of moles, n.*

$$V \propto n \qquad \text{(at constant } T \text{ and } P\text{)}$$

Standard Molar Volume

Avogadro's principle implies that the volume occupied by one mole of *any* gas—its *molar volume*—must be identical for all gases under the same conditions of pressure and temperature. To compare the molar volumes of different gases, scientists agreed to use 1 atm

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[5] The great French chemist Antoine Laurent Lavoisier (1743–1794) was the first to observe the volume relationships of this particular reaction. In his 1789 textbook, *Elements of Chemistry,* he wrote that the formation of water from hydrogen and oxygen requires that two volumes of hydrogen be used for every volume of oxygen. Lavoisier was unable to extend the study of this behavior of hydrogen and oxygen to other gas reactions because he was beheaded during the French Revolution. (See Michael Laing, *The Journal of Chemical Education,* February 1998, page 177.)

Table 11.1 Molar Volumes of Some Gases at STP

Gas	Formula	Molar Volume (L)
Helium	He	22.398
Argon	Ar	22.401
Hydrogen	H_2	22.410
Nitrogen	N_2	22.413
Oxygen	O_2	22.414
Carbon dioxide	CO_2	22.414

and 273.15 K (0 °C) as the **standard conditions of temperature and pressure**,[6] or **STP**, for short. If we measure the molar volumes for a variety of gases at STP, we find that the values fluctuate somewhat because the gases are not "ideal." Some typical values are listed in Table 11.1, and if we were to examine the data for many gases we would find an average of around 22.4 L per mole. This value is taken to be the molar volume of an *ideal gas* at STP and is now called the **standard molar volume** of a gas.

For an ideal gas at STP:

$$1 \text{ mol gas} \Leftrightarrow 22.4 \text{ L gas}$$

Avogadro's principle was a remarkable advance in our understanding of gases. His insight enabled chemists for the first time to determine the formulas of gaseous elements.[7]

Stoichiometry Problems

For reactions involving gases, Avogadro's principle lets us use a new kind of stoichiometric equivalency, one between *volumes* of gases. Earlier, for example, we noted the following reaction and its gas volume relationships.

$$\underset{2 \text{ volumes}}{2H_2(g)} + \underset{1 \text{ volume}}{O_2(g)} \longrightarrow \underset{2 \text{ volumes}}{2H_2O(g)}$$

Provided we are dealing with gas volumes measured at the same temperature and pressure, we can write the following stoichiometric equivalencies.

$$2 \text{ volumes } H_2(g) \Leftrightarrow 1 \text{ volume } O_2(g) \quad \text{just as} \quad 2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2$$
$$2 \text{ volumes } H_2(g) \Leftrightarrow 2 \text{ volumes } H_2O(g) \quad \text{just as} \quad 2 \text{ mol } H_2 \Leftrightarrow 2 \text{ mol } H_2O$$
$$1 \text{ volume } O_2(g) \Leftrightarrow 2 \text{ volumes } H_2O(g) \quad \text{just as} \quad 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

Relationships such as these can greatly simplify stoichiometry problems, as we see in Example 11.3.

■ The recognition that equivalencies in gas *volumes* are numerically the same as those for numbers of moles of gas in reactions involving gases simplifies many calculations.

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[6] Today there are more than a dozen definitions of "standard temperature and pressure." Our selection of STP is predicated on tradition and the fact that pressure, commonly measured in mm Hg from a manometer, is easily converted to atmospheres.

[7] Suppose that hydrogen chloride, for example, is correctly formulated as HCl, not as H_2Cl_2 or H_3Cl_3 or higher, and certainly not as $H_{0.5}Cl_{0.5}$. Then the only way that *two* volumes of hydrogen chloride could come from just *one* volume of hydrogen and *one* of chlorine is if each particle of hydrogen and each of chlorine were to consist of *two* atoms of H and Cl, respectively, H_2 and Cl_2. If these particles were single-atom particles, H and Cl, then one volume of H and one volume of Cl could give only *one* volume of HCl, not two. Of course, if the initial assumption were incorrect so that hydrogen chloride is, say, H_2Cl_2 instead of HCl, then hydrogen would be H_4 and chlorine would be Cl_4. The extension to larger subscripts works in the same way.

Example 11.3
Stoichiometry of Reactions of Gases

How many liters of hydrogen, $H_2(g)$, measured at STP, are needed to combine exactly with 1.50 L of nitrogen, also measured at STP, to form ammonia?

Analysis: The problem states that the reactants are at STP, standard temperature (273 K) and pressure (760 torr). Therefore all the gases in this example are at the same temperature and pressure. That makes the ratios by volume the same as the ratio by moles, which means that the ratios by volume are the same as the ratios of the coefficients of the balanced equation. So we can then substitute the volume ratio for the mole ratio in our calculations.

Assembling the Tools: We're dealing with a chemical reaction, so we need the balanced chemical equation we learned to construct in Chapter 3.

$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$

Avogadro's principle then gives us the equivalency we need to perform the calculation.

$$3 \text{ volumes } H_2 \Leftrightarrow 1 \text{ volume } N_2$$

The stoichiometric procedures learned in Chapter 4 can be used to solve the problem.

Solution: We now restate the problem as

$$1.50 \text{ L } N_2 \Leftrightarrow ? \text{ L } H_2$$

We use the volume ratio, now in L units, to express the equivalence

$$3 \text{ L } H_2 \Leftrightarrow 1 \text{ L } N_2$$

This volume equivalence is used to construct the conversion factor, and our solution is

$$1.50 \cancel{\text{ L } N_2} \times \frac{3 \text{ L } H_2}{1 \cancel{\text{ L } N_2}} = 4.50 \text{ L } H_2$$

Is the Answer Reasonable? The volume of H_2 needed is three times the volume of N_2, and 3 × 1.5 equals 4.5, so the answer is correct. Remember, however, that the simplicity of this problem arises because the volumes are at the same temperature and pressure.

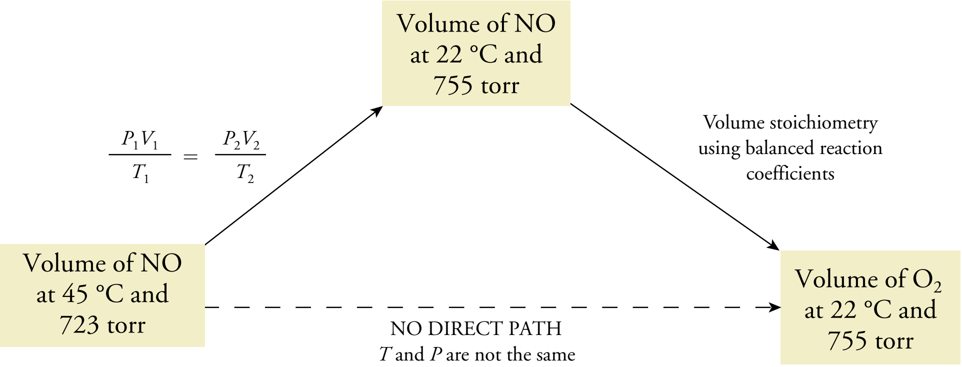
Example 11.4
Stoichiometry Calculations when Gases Are Not at the Same *T* and *P*

Nitrogen monoxide, a pollutant released by automobile engines, is oxidized by molecular oxygen to give the reddish-brown gas nitrogen dioxide, which gives smog its characteristic color. The equation is

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

How many milliliters of O_2, measured at 22 °C and 755 torr, are needed to react with 184 mL of NO, measured at 45 °C and 723 torr?

Analysis: Once again, we have a stoichiometry problem involving gas volumes, but this one is more complicated than the one in Example 11.3 because the gases are not at the same temperature and pressure. The way to resolve this difficulty is to make the temperature and pressure the same for both gases. Since we are asked for the volume of O_2 at 22 °C and 755 torr, it will be easiest if we determine the volume of the NO under those conditions. Once we do that, we can use the gas volumes for our stoichiometry calculation as diagrammed below.


Volume of NO at 22 °C and 755 torr
$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
Volume stoichiometry using balanced reaction coefficients
Volume of NO at 45 °C and 723 torr
Volume of O_2 at 22 °C and 755 torr
NO DIRECT PATH
T and P are not the same

With that analysis, this problem is seen to contain two concepts: the *combined gas law* and a *stoichiometry calculation* using gas volumes.

Assembling the Tools: We can use the combined gas law to find what volume the NO would occupy if it were at the same temperature and pressure as the O_2. Then we can use the coefficients of the equation to find the volume of O_2.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

We will again use Avogadro's principle once the volumes at the same temperature and pressure are determined.

Solution: We use the combined gas law applied to the given volume of NO, so let's set up the data as usual.

	Initial (1)			**Final (2)**	
P_1	723 torr		P_2	755 torr	
V_1	184 mL		V_2	?	
T_1	318 K	(45 °C + 273)	T_2	295 K	(22 °C + 273)

Solving the combined gas law for V_2 gives

$$V_2 = V_1 \times \left(\frac{P_1}{P_2}\right) \times \left(\frac{T_2}{T_1}\right)$$

Next we substitute values:

$$\begin{aligned} V_2 &= 184 \text{ mL} \times \left(\frac{723 \cancel{\text{ torr}}}{755 \cancel{\text{ torr}}}\right) \times \left(\frac{295 \cancel{\text{ K}}}{318 \cancel{\text{ K}}}\right) \\ &= 163.5 \text{ mL NO} \end{aligned}$$

We can now use the coefficients of the equation to establish the equivalency

$$2 \text{ mL NO} \Leftrightarrow 1 \text{ mL } O_2$$

and apply it to find the volume of O_2 required for the reaction.

$$163.5 \cancel{\text{ mL NO}} \times \frac{1 \text{ mL } O_2}{2 \cancel{\text{ mL NO}}} = 81.7 \text{ mL } O_2$$

Note how we kept an extra significant figure in V_2 until we calculated the final volume of O_2.

Is the Answer Reasonable? For the first calculation, we can check to see whether the pressure and temperature ratios move the volume in the right direction. The pressure is increasing (723 torr ⟶ 755 torr), so that should decrease the volume. The pressure ratio is smaller than 1, so it is having the proper effect. The temperature is dropping (318 K ⟶ 295 K), so this change should also reduce the volume. The temperature ratio is smaller than 1, so it is also having the correct effect. The volume of NO at 22 °C and 755 torr is probably correct. We can also observe that the two ratios are only slightly less than 1.0 and we expect the answer to be close to the given volume, which it is.

The check of the calculation is simple. According to the equation, the volume of O_2 required should be half the volume of NO, which it is, so the final answer seems to be okay.

Practice Exercises

11.8 | Methane burns according to the following equation.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

The combustion of 4.50 L of CH_4 consumes how many liters of O_2, both volumes measured at 25 °C and 740 torr? (*Hint:* Recall Avogadro's principle concerning the number of molecules in a fixed volume of gas at a given temperature and pressure.)

11.9 | How many liters of air (air is 20.9% oxygen) are required for the combustion of 6.75 L of CH_4?

11.10 | The multi-step problem in Example 11.4 can be solved by calculating the volume of oxygen at the initial T and P of the NO and then using the combined gas law to calculate the volume of oxygen at the desired T and P (i.e., we can switch the sequence of the steps). Verify that you get the same answer using this method.

11.5 | Ideal Gas Law

In our discussion of the combined gas law, we noted that the ratio PV/T equals a constant for a fixed amount of gas. However, the value of this "constant" is actually proportional to the number of moles of gas, n, in the sample.[8]

To create an equation even more general than the combined gas law, therefore, we can write

$$\frac{PV}{T} \propto n$$

We can replace the proportionality symbol with an equals sign by including another proportionality constant.

$$\frac{PV}{T} = n \times \text{constant}$$

This new constant is given the symbol ***R*** and is called the **universal gas constant.** We can now write the combined gas law in a still more general form called the **ideal gas law.**

Sometimes this equation is called the *universal gas law.*

$$\frac{PV}{T} = nR$$

---

[8] In the problems we worked earlier, we were able to use the combined gas law expressed as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

because the amount of gas remained fixed.

An ideal gas would obey this law exactly over all ranges of the gas variables. The equation, sometimes called the **equation of state for an ideal gas**, is usually rearranged and written as follows.

Ideal Gas Law (Equation of State for an Ideal Gas)

$$PV = nRT \tag{11.2}$$

TOOLS

Ideal gas law

Equation 11.2 tells us how the four important variables for a gas, P, V, n, and T, are related. If we know the values of three, we can calculate the fourth. In fact, Equation 11.2 tells us that if values for three of the four variables are fixed for a given gas, *the fourth can only have one value*. We can define the *state* of a given gas simply by specifying any three of the four variables P, V, T, and n.

■ If n, P, and T in Equation 11.2 are known, for example, then V can have *only one value.*

To use the ideal gas law, we have to know the value of the universal gas constant, R, which is equal to PV/nT. The value of R will depend on the values and units we choose for P, V, T, and n. We will use units of liters for volume, kelvins for temperature, atmospheres for temperature, and moles for n. Earlier, on page 487 we defined the standard temperature and pressure, STP, as 273 K and one atmosphere of pressure. We also noted that one mole of an ideal gas has a volume of 22.4 liters. Using these values we can calculate R as follows.

■ More precise measurements give $R = 0.082057$ L atm mol^{-1} K^{-1}. If we use the bar as the standard pressure, then $R = 0.083144$ L bar mol^{-1} K^{-1}.

$$R = \frac{PV}{nT} = \frac{(1.00\ \text{atm})(22.4\ \text{L})}{(1.00\ \text{mol})(273\ \text{K})}$$

$$= 0.0821\ \frac{\text{atm L}}{\text{mol K}}$$

or, arranging the units in a commonly used order,

$$\boldsymbol{R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}}$$

To use this value of R in working problems, we have to be sure to express volumes in liters, temperatures in kelvins, and pressures in atmospheres. In later chapters we will find R defined using different units, and, of course, it will have a different numerical value.

Example 11.5
Using the Ideal Gas Law

In Example 11.2, we described filling a 158 mL light bulb with argon at a temperature of 21 °C and a pressure of 3.00 torr. How many grams of argon are in the light bulb under these conditions?

■ **Analysis:** The question asks for the grams of Ar, and our stoichiometry experience (see Figure 4.6 on page 142) tells us that the only way to calculate the mass of Ar is first to know the moles of Ar (or some way to calculate the moles of Ar). The first step will be to determine the moles of Ar in the light bulb; then we will convert moles to mass.

■ **Assembling the Tools:** The only equation that allows us to calculate the moles of a gas is the ideal gas law equation, $PV = nRT$. We will solve it for n by substituting values for P, V, R, and T. Once we have the number of moles of Ar, the tool to use is the relationship of atomic mass to moles. For Ar we write

$$1\ \text{mol Ar} = 39.95\ \text{g Ar}$$

A conversion factor $\dfrac{39.95\ \text{g Ar}}{1\ \text{mol Ar}}$ made from this relationship lets us convert moles to grams.

■ **Solution:** When using the ideal gas law we need to be sure that P, V, and T have the correct units. One helpful clue is that the units for R must cancel and therefore they prescribe the units we need for our variables. When using $R = 0.0821$ L atm mol^{-1} K^{-1}, we must have V in liters, P in atmospheres, and T in kelvins. Gathering the data and making the necessary unit conversions as we go, we have

$$\begin{array}{ll} P = 3.95 \times 10^{-3}\ \text{atm} & \text{from } 3.00\ \cancel{\text{torr}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{torr}}} \\ V = 0.158\ \text{L} & \text{from } 158\ \text{mL} \\ T = 294\ \text{K} & \text{from } (21\ {}^\circ\text{C} + 273) \end{array}$$

Rearranging the ideal gas law for n gives us

$$n = \frac{PV}{RT}$$

Substituting the proper values of P, V, R, and T into this equation gives

$$\begin{aligned} n &= \frac{(3.95 \times 10^{-3}\ \cancel{\text{atm}})(0.158\ \cancel{\text{L}})}{(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(294\ \cancel{\text{K}})} \\ &= 2.59 \times 10^{-5}\ \text{mol of Ar} \end{aligned}$$

Now we convert moles of Ar to grams of Ar. Let's set up the question as an equation:

$$2.59 \times 10^{-5}\ \text{mol of Ar} = ?\ \text{g Ar}$$

Then we use the conversion factor above to complete the calculation.

$$2.59 \times 10^{-5}\ \cancel{\text{mol Ar}} \times \frac{39.95\ \text{g Ar}}{1\ \cancel{\text{mol Ar}}} = 1.04 \times 10^{-3}\ \text{g Ar}$$

Thus, the light bulb contains only about one milligram of argon.

■ **Is the Answer Reasonable?** As in other problems we approximate the answer by rounding all values to one significant figure to get:

$$n = \frac{(4 \times 10^{-3}\ \text{atm})(0.2\ \text{L})}{(0.1\ \text{L atm mol}^{-1}\ \text{K}^{-1})(300\ \text{K})} = \frac{(0.8 \times 10^{-3}\ \text{mol})}{(30)} \approx 3 \times 10^{-5}\ \text{mol}$$

This is close to our answer for the moles of argon.

We multiply the estimate above by 40 g Ar/mol Ar to get 1×10^{-3} grams. The result is very close to our calculated value. (Whenever you're working a problem where there is unit cancellation, be sure to check to be sure that the units do cancel as they are supposed to by adding your own cancellations here.)

Practice Exercises

11.11 | Dry ice, solid $CO_2(s)$, can be made by allowing pressurized $CO_2(g)$ to expand rapidly. If 35% of the expanding $CO_2(g)$ ends up as $CO_2(s)$, how many grams of dry ice can be made from a tank of $CO_2(g)$ that has a volume of 6.0 cubic feet with a gauge pressure of 2.00×10^3 pounds per square inch (PSIG) at 22 °C? (*Hint:* The information in the table on page 476 will help set up the conversions needed. *Note:* PSIG is the pressure above the prevailing atmospheric pressure that we can assume is 1.00 atm.)

11.12 | How many grams of argon were in the 12.0 L cylinder of argon used to fill the light bulbs described in Example 11.2? The pressure of the argon was 57.8 atm and the temperature was 25 °C.

Calculating Molar Mass

When a chemist makes a new compound, its molar mass is usually determined to help establish its chemical identity. In general, *to determine the molar mass of a compound experimentally, we need to find two pieces of information about a given sample—the mass of the sample and the number of moles of the substance in the sample*. Once we have mass and moles for the same sample, we simply divide the number of grams by the number of moles to find the molar mass. For instance, if we had a sample weighing 6.40 g and found that it also contained 0.100 mol of the substance, the molar mass would be

$$\frac{6.40 \text{ g}}{0.100 \text{ mol}} = 64.0 \text{ g mol}^{-1}$$

TOOLS

Determination of molar mass from the ideal gas law

■ Recall that when the molecular mass of a substance is expressed in units of grams per mole, the quantity is called the *molar mass.*

If the compound is a gas, its molar mass can be found using experimental values of pressure, volume, temperature, and sample mass. The P, V, T data allow us to calculate the number of moles using the ideal gas law (as in Example 11.5). Once we know the number of moles of gas and the mass of the gas sample, the molar mass is obtained by taking the ratio of *grams to moles*.

Example 11.6
Determining the Molar Mass of a Gas

As part of a rock analysis, a student added hydrochloric acid to a rock sample and observed a fizzing action, indicating that a gas was being evolved (see the figure in the margin). The student collected a sample of the gas in a 0.220 L gas bulb until its pressure reached 0.757 atm at a temperature of 25.0 °C. The sample weighed 0.299 g. What is the molar mass of the gas? What kind of compound was the likely source of the gas?

Hydrochloric acid reacting with a rock sample. *(Andy Washnik)*

■ **Analysis:** The strategy for finding the molar mass was described previously. We use the P, V, T data to calculate the number of moles of gas in the sample. Then we divide the mass by the number of moles to find the molar mass.

■ **Assembling the Tools:** The first tool is the ideal gas law that we use to solve for n,

$$n = \frac{PV}{RT}$$

The next tool is the definition of the molar mass,

$$\text{molar mass} = \frac{\text{mass of sample}}{\text{moles in sample}}$$

■ **Solution:** Any use of the ideal gas law requires the correct units. The pressure given is already in atmospheres and the volume is in liters, but we must convert degrees Celsius into kelvins. Gathering our data, we have

$$P = 0.757 \text{ atm} \qquad V = 0.220 \text{ L} \qquad T = 298 \text{ K} \quad (25.0\ ^\circ\text{C} + 273)$$

Now we can substitute the data for P, V, and T, along with the value of R. This gives

$$\begin{aligned} n &= \frac{(0.757\ \cancel{\text{atm}})(0.220\ \cancel{\text{L}})}{(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(298\ \cancel{\text{K}})} \\ &= 6.81 \times 10^{-3} \text{ mol} \end{aligned}$$

The molar mass is obtained from the ratio of grams to moles:

$$\text{molar mass} = \frac{0.299 \text{ g}}{6.81 \times 10^{-3} \text{ mol}} = 43.9 \text{ g mol}^{-1}$$

We now know the measured molar mass is 43.9, but what gas could this be? Looking back on our discussions in Chapter 5, what gases do we know are given off when a substance reacts with acids? On page 181 we find some options; the gas might be H_2S, HCN, CO_2, or SO_2. Using atomic masses to calculate their molar masses, we get

H_2S	34 g mol^{-1}	CO_2	44 g mol^{-1}
HCN	27 g mol^{-1}	SO_2	64 g mol^{-1}

The only gas with a molar mass close to 43.9 is CO_2, and that gas would be evolved if we treat a carbonate with an acid. The rock probably contains a carbonate compound. (Limestone and marble are examples of such minerals.)

■ **Are the Answers Reasonable?** We don't have to do much mental arithmetic to gain some confidence in our answer. The volume of the gas sample (0.220 L) is a bit less than 1/100 of 22.4 L, the volume of one mole at STP. If the gas were at STP, then 0.299 g would be 1/100 of a mole, so an entire mole would weigh about 30 g (rounded from 29.9 g). Although 30 g per mole is not very close to 43.9 g per mole, we do appear to have the decimal in the right place. We can refine our estimate a bit. We see that the temperature is within 10% of the standard temperature and has a minor effect, but the pressure is only 75% of atmospheric pressure and is the major reason why our first estimate was off. Dividing the estimated molar mass by 0.75 (or multiplying by 1.33) gives an estimated answer of 40, very close to the one we calculated. In addition, the fact that the answer (43.9 g mol^{-1}) agrees so well with the molar mass of one of the gases formed when substances react with acids makes all the puzzle pieces fit. Viewed in total, therefore, we can feel confident in our answers.

Practice Exercises

11.13 | A glass bulb is found to have a volume of 544.23 mL. The mass of the glass bulb filled with argon is 735.6898 g. The bulb is then flushed with a gaseous organic compound. The bulb, now filled with the organic gas, weighs 736.1310 g. The measurements were made at STP. What is the molar mass of the organic gas? (*Hint:* Calculate the difference in molar masses.)

11.14 | The label on a cylinder of a noble gas became illegible, so a student allowed some of the gas to flow into an evacuated gas bulb with a volume of 300.0 mL until the pressure was 685 torr. The mass of the glass bulb increased by 1.45 g; its temperature was 27.0 °C. What is the molar mass of this gas? Which of the Group 8A gases was it?

Gas Densities

■ Recall from Chapter 2 that density is the ratio of mass to volume. For liquids and solids, we usually use units of g mL^{-1} (or g cm^{-3}), but because gases have such low densities, units of g L^{-1} give numbers that are easier to comprehend.

Because one mole of any gas occupies the same volume at a particular pressure and temperature, the mass contained in that volume depends on the molar mass of the gas. Consider, for example, one-mole samples of O_2 and CO_2 at STP (Figure 11.9). Each sample occupies a volume of 22.4 L. The oxygen sample has a mass of 32.0 g while the carbon dioxide sample has a mass of 44.0 g. If we calculate the densities of the gases, we find the density of CO_2 is larger than that of O_2.

$$d_{O_2} = \frac{32.0\ \text{g}}{22.4\ \text{L}} = 1.43\ \text{g L}^{-1} \qquad d_{CO_2} = \frac{44.0\ \text{g}}{22.4\ \text{L}} = 1.96\ \text{g L}^{-1}$$

Because the volume of a gas is affected by temperature and pressure, the density of a gas changes as these variables change. Gases become less dense as their temperatures rise, which is why hot-air balloons are able to float; the less dense hot air inside the balloon floats in the more dense cool air that surrounds it. Gases also become more dense as their pressures increase because increasing the pressure packs more molecules into the same space. To calculate the density of a gas at conditions other than STP, we use the ideal gas law, as illustrated in Example 11.7.

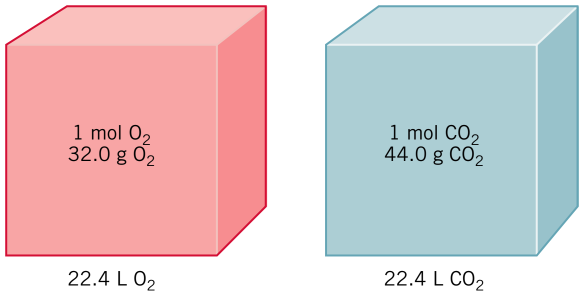


Figure 11.9 | **One-mole samples of O_2 and CO_2 at STP.** Each sample occupies 22.4 L, but the O_2 weighs 32.0 g whereas the CO_2 weighs 44.0 g. The CO_2 has more mass per unit volume than the O_2 and has the higher density.

Example 11.7
Calculating the Density of a Gas

One procedure used to separate the isotopes of uranium to obtain material to construct a nuclear weapon employs a uranium compound with the formula UF_6. The compound boils at about 56 °C, so at 95 °C it is a gas. What is the density of UF_6 at 95 °C if the pressure of the gas is 746 torr? (Assume the gas contains the mix of uranium isotopes commonly found in nature.)

■ **Analysis:** The ideal gas law has all of the information needed to calculate the density of a gas. We will need to combine two concepts, the ideal gas law and the density of materials. Sometimes it is easier to combine equations before doing any calculations, as we will do here.

■ **Assembling the Tools:** We will need the ideal gas law and the equations for calculating the number of moles, n, and the density, d. Those equations are

$$n = \frac{\text{mass}}{\text{molar mass}} \quad \text{and} \quad d = \frac{\text{mass}}{\text{volume}}$$

In many instances we need to convert units, so we should be prepared to convert between torr and atmospheres as well as from °C to K.

■ **Solution:** To combine the two concepts we will substitute the equation for n above into the ideal gas law (Equation 11.2) to get

$$PV = \frac{\text{mass}}{\text{molar mass}} \times RT$$

Now we rearrange the equation to the form for density

$$\frac{P \times \text{molar mass}}{RT} = \frac{\text{mass}}{V} = d$$

The right side of this equation is the density. After converting 746 torr to 0.9816 atm and 95 °C to 368 K we enter the data into the equation along with the molar mass of 352.0 g/mol for UF_6 as

$$\frac{(0.9816\ \cancel{\text{atm}})(352.0\ \text{g UF}_6/\cancel{\text{mol}}\ \text{UF}_6)}{(0.0821\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(368\ \cancel{\text{K}})} = d = 11.3\ \text{g/L}$$

The density of gaseous UF_6 is 11.3 g/L.

■ **Is the Answer Reasonable?** At STP, the density would be equal to 352 g ÷ 22.4 L = 15.7 g L^{-1}. The given pressure is almost 1 atm, but the temperature is quite a bit higher than 273 K. Gases expand when heated, so a liter of the gas at the higher temperature will have less UF_6 in it. That means the density will be lower at the higher temperature, and our answer agrees with this analysis. Our answer is reasonable.

Practice Exercises

11.15 | Radon, a radioactive gas, is formed in one step of the natural radioactive decay sequence of U-235 to Pb-207. Radon usually escapes harmlessly through the soil to the atmosphere. When the soil is frozen or saturated with water the only escape route is through cracks in the basements of houses and other buildings. In order to detect radon in a residence, would you place the sensor in the attic, the ground floor living area, or the basement? Justify your answer. (*Hint:* Compare the approximate density of air, 1.3 g L^{-1}, to the density of radon.)

11.16 | Sulfur dioxide is a gas that has been used in commercial refrigeration, but not in residential refrigeration because it is toxic. If your refrigerator used SO_2, you could be injured if it developed a leak. What is the density of SO_2 gas measured at -5 °C and a pressure of 96.5 kPa?

Calculating Molar Mass from Gas Density

One of the ways we can use the density of a gas is to determine the molar mass. To do this, we also need to know the temperature and pressure at which the density was measured. Example 11.8 illustrates the reasoning and calculation involved.[9]

Example 11.8
Calculating the Molecular Mass from Gas Density

A liquid sold under the trade name Perclene is used as a dry cleaning solvent. It has an empirical formula CCl_2 and a boiling point of 121 °C. When vaporized, the gaseous compound has a density of 4.93 g L^{-1} at 785 torr and 155 °C. What is the molar mass of the compound and what is its molecular formula?

■ **Analysis:** In Example 11.7 we saw how the density could be calculated using the ideal gas law if we knew P, T, and the molar mass. Knowing the density suggests we can calculate the molar mass. When we know the empirical formula and the molar mass we can determine the molecular formula.

■ **Assembling the Tools:** Again, we need to combine two concepts, the ideal gas law and the density. We can use the information in Example 11.7 to write

$$d = \frac{P \times \text{molar mass}}{RT}$$

---

[9] From the ideal gas law we can derive an equation from which we could calculate the molar mass directly from the density. If we let the mass of gas equal g, we could calculate the number of moles, n, by the ratio

$$n = \frac{g}{\text{molar mass}}$$

Substituting into the ideal gas law gives

$$PV = nRT = \frac{gRT}{\text{molar mass}}$$

Solving for molar mass, we have

$$\text{molar mass} = \frac{gRT}{PV} = \left(\frac{g}{V}\right) \times \frac{RT}{P}$$

The quantity g/V is the ratio of mass to volume, which is the density d, so making this substitution gives

$$\text{molar mass} = \frac{dRT}{P}$$

This equation could also be used to solve the problem in Example 11.8 by substituting values for d, R, T, and P.

As usual, we will be prepared to convert torr to atmospheres and °C to K temperature units. Finally, we add in the third concept involved in this question, the determination of molecular formulas. For this we use the tool found in Section 4.3.

■ **Solution:** Rearranging the equation above to solve for molar mass gives us

$$\text{molar mass} = \frac{dRT}{P}$$

To perform this calculation and cancel the units of R correctly we need to have the pressure in atmosphere units and the temperature in kelvins.

$$\begin{aligned} T &= 428\ \text{K} && \text{from } (155\ ^\circ\text{C} + 273) \\ P &= 1.03\ \text{atm} && \text{from } 785\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} \\ V &= 1.00\ L && \end{aligned}$$

Then

$$\text{molar mass} = \frac{(4.93\ \text{g}\ \cancel{\text{L}^{-1}})(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(428\ \cancel{\text{K}})}{(1.03\ \cancel{\text{atm}})}$$

$$\text{molar mass} = 168\ \text{g mol}^{-1}$$

To calculate the molecular formula, we divide the empirical formula mass into the molecular mass to see how many times CCl_2 occurs in the molecular formula. The empirical formula mass of CCl_2 is 82.9. We now divide the molar mass by this value:

$$\frac{168}{82.9} = 2.03$$

The result is close enough to 2.00, so to find the molecular formula, we multiply all of the subscripts of the empirical formula by 2:

$$\text{molecular formula} = C_{1\times 2}Cl_{2\times 2} = C_2Cl_4$$

(This is the formula for a compound commonly called tetrachloroethylene, which is indeed used as a dry cleaning fluid.)

■ **Is the Answer Reasonable?** Sometimes we don't have to do any arithmetic to see that an answer is almost surely correct. The fact that the molar mass we calculated from the gas density is evenly divisible by the empirical formula mass suggests we've worked the problem correctly.

Practice Exercises

11.17 | A gaseous compound of phosphorus and fluorine with an empirical formula of PF_2 has a density of 5.60 g L^{-1} at 23.0 °C and 750 torr. Determine the molecular formula of this compound. (*Hint:* Calculate the molar mass from the density.)

11.18 | A compound composed of only carbon and hydrogen has a density of 5.55 g/L at 40.0 °C and 1.25 atm. What is the molar mass of the compound? What are the possible combinations of C and H that add up to that molar mass? Using the information in Section 2.6, determine which of your formulas is most likely the correct one.

Stoichiometry Using the Ideal Gas Law

Many chemical reactions either consume or give off gases. The ideal gas law can be used to relate the volumes of such gases to the amounts of other substances involved in the reaction, as illustrated by the following example.

Example 11.9

Calculating the Volume of a Gaseous Product Using the Ideal Gas Law

An important chemical reaction in the manufacture of Portland cement is the high temperature decomposition of calcium carbonate to give calcium oxide and carbon dioxide.

$$CaCO_3(s) \longrightarrow CO_2(g) + CaO(s)$$

Suppose a 1.25 g sample of $CaCO_3$ is decomposed by heating. How many milliliters of CO_2 gas will be evolved if the volume will be measured at 745 torr and 25 °C?

Analysis: This appears to be a stoichiometry problem where we must to convert the mass of one substance into the volume of a gas that would be expected from the reaction.

Assembling the Tools: We need to assemble all of the techniques we used for stoichiometry calculations in Section 4.4. In addition we will need the ideal gas law to convert the moles of gaseous product into the expected volume of gas. The specific relationships we need are

$$1 \text{ mol } CaCO_3 \Leftrightarrow 1 \text{ mol } CO_2$$

$$1 \text{ mol } CaCO_3 = 100.1 \text{ g } CaCO_3$$

Our sequence of conversions will be

$$\text{g } CaCO_3 \longrightarrow \text{mol } CaCO_3 \longrightarrow \text{mol } CO_2 \longrightarrow \text{mL } CO_2$$

Solution: First, we will convert the 1.25 g of $CaCO_3$ to moles of $CaCO_3$, which is then converted to the number of moles of CO_2. We will use this value for n in the ideal gas law equation to find the volume of CO_2.

The formula mass of $CaCO_3$ is 100.1, so

$$\begin{aligned}\text{moles of } CaCO_3 &= 1.25 \cancel{\text{g}} \; CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \cancel{\text{g}} \; CaCO_3} \\ &= 1.25 \times 10^{-2} \text{ mol } CaCO_3\end{aligned}$$

Because 1 mol $CaCO_3 \Leftrightarrow$ 1 mol CO_2 we must have 1.25×10^{-2} mol CO_2, which we will use for n in the ideal gas law.

Before we use n in the ideal gas law equation, we must convert the given pressure and temperature into the units required by R.

$$P = 745 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 0.980 \text{ atm} \qquad T = (25.0 \text{ °C} + 273) = 298 \text{ K}$$

By rearranging the ideal gas law equation we obtain

$$\begin{aligned}V &= \frac{nRT}{P} \\ &= \frac{(1.25 \times 10^{-2} \cancel{\text{mol}})(0.0821 \text{ L} \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}})(298 \cancel{\text{K}})}{0.980 \cancel{\text{atm}}} \\ &= 0.312 \text{ L} = 312 \text{ mL}\end{aligned}$$

The reaction will yield 312 mL of CO_2 at the conditions specified.

Is the Answer Reasonable? We round all of the numbers in our calculation to one significant figure to get (cancel the units in the setup below)

$$V = \frac{(1 \times 10^{-2} \text{ mol})(0.1 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{1 \text{ atm}} = 0.3 \text{ L} \quad \text{or} \quad 300 \text{ mL}$$

This answer is close to what we calculated above, and we may assume the calculation is correct. We also note that all units cancel to leave the desired liter units for volume.

Practice Exercises

11.19 | Carbon disulfide is an extremely flammable liquid. It can be ignited by any small spark or even a very hot surface such as a steam pipe. The combustion reaction is

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$$

When 11.0 g of CS_2 are burned in excess oxygen, how many liters of CO_2 and SO_2 are formed at 28 °C and 883 torr? (*Hint:* Treat this as an ordinary stoichiometry problem.)

11.20 | In one lab, the gas-collecting apparatus used a gas bulb with a volume of 257 mL. How many grams of $CaCO_3(s)$ need to be heated to prepare enough $CO_2(g)$ to fill this bulb to a pressure of 738 torr at a temperature of 23 °C? The equation is

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

11.6 | Dalton's Law of Partial Pressures

So far in our discussions we've dealt with only pure gases. However, gas mixtures, such as the air we breathe, are quite common. In general, gas mixtures obey the same laws as pure gases, so Boyle's law applies equally to both pure oxygen and to air. There are times, though, when we must be concerned with the composition of a gas mixture, such as when we are studying a pollutant in the atmosphere. In these cases, the variables affected by the composition of a gas mixture are the numbers of moles of each component and the contribution each component makes to the total observed pressure. Because gases mix completely, all the components of the mixture occupy the same volume—that of the container holding them. Furthermore, the temperature of each gaseous component is the same as the temperature of the entire mixture. Therefore, in a gas mixture, each of the components has the same volume and the same temperature.

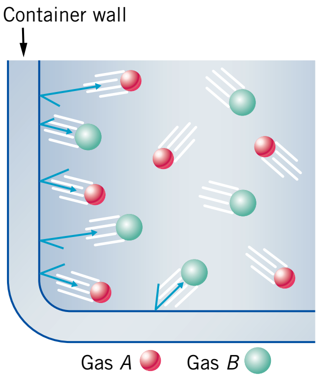


Figure 11.10 | **Partial pressures viewed at the molecular level.** In a mixture of two gases, *A* and *B*, both collide with the walls of the container and thereby contribute their partial pressures to the total pressure.

Partial Pressures

In a mixture of nonreacting gases such as air, each gas contributes to the total pressure in proportion to the fraction (by moles) in which it is present (see Figure 11.10). This contribution to the total pressure is called the **partial pressure** of the gas. It is the pressure the gas would exert if it were the only gas in a container of the same size at the same temperature.

■ Under ordinary temperatures and pressures, nitrogen and oxygen in air do not react.

The general symbol we will use for the partial pressure of a gas A is P_A. For a particular gas, the formula of the gas may be put into the subscript, as in P_{O_2}. What John Dalton discovered about partial pressures is now called **Dalton's law of partial pressures**: *The total pressure of a mixture of gases is the sum of their individual partial pressures.* In equation form, the law is

$$P_{\text{total}} = P_A + P_B + P_C + \cdots \qquad \textbf{(11.3)}$$

TOOLS

Dalton's law of partial pressures

In dry CO_2-free air at STP, for example, P_{O_2} is 159.12 torr, P_{N_2} is 593.44 torr, and P_{Ar} is 7.10 torr. These partial pressures add up to 759.66 torr, just 0.34 torr less than 760 torr or 1.00 atm. The remaining 0.34 torr is contributed by several trace gases, including other noble gases.

Practice Exercises

11.21 | At 28 °C a 1.00 liter flask is filled with 11.0 g of Ar, 10.6 g of N_2, and 14.3 g of O_2. What are the partial pressures of each gas, and what is the total pressure in the flask? (*Hint:* Start by calculating the moles of each gas present.)

11.22 | Suppose a tank of oxygen-enriched air prepared for scuba diving has a volume of 17.00 L and a pressure of 237.0 atm at 25 °C. How many grams of oxygen are present if all the other gases in the tank exert a partial pressure of 115.0 atm?

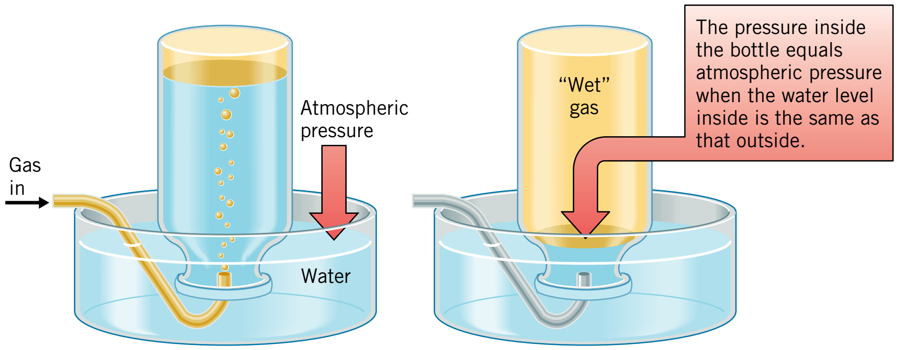

Gas in
Atmospheric pressure
Water
"Wet" gas
The pressure inside the bottle equals atmospheric pressure when the water level inside is the same as that outside.

Figure 11.11 | **Collecting a gas over water.** As the gas bubbles through the water, water vapor goes into the gas, so the total pressure inside the bottle includes the partial pressure of the water vapor at the temperature of the water.

Collecting Gases over Water

When gases that do not react with water are prepared in the laboratory, they can be trapped over water by an apparatus like that shown in Figure 11.11. Because of the way the gas is collected, it is saturated with water vapor. (We say the gas is "wet.") Water vapor in a mixture of gases has a partial pressure like that of any other gas.

■ Even the mercury in a barometer has a tiny vapor pressure—0.0012 torr at 20 °C—which is much too small to affect readings of barometers and the manometers studied in this chapter.

The vapor present in the space above *any* liquid always contains some of the liquid's vapor, which exerts its own pressure called the liquid's **vapor pressure.** Its value for any given substance depends only on the temperature. The vapor pressures of water at different temperatures, for example, are listed in Table 11.2. A more complete table is in Appendix C. 5.

If we have adjusted the height of the collecting jar so the water level inside matches that outside, the total pressure of the trapped gas equals the atmospheric pressure, so the value for P_{total} is obtained from the laboratory barometer. We can now calculate P_{gas}, which is the pressure that the gas would exert if it were dry (i.e., without water vapor in it) and inside the same volume that was used to collect it.[10]

Table 11.2 Vapor Pressure of Water at Various Temperatures[a]

Temperature (°C)	Vapor Pressure (torr)	Temperature (°C)	Vapor Pressure (torr)
0	4.579	50	92.51
5	6.543	55	118.0
10	2.209	60	149.4
15	12.79	65	187.5
20	17.54	70	233.7
25	23.76	75	289.1
30	31.82	80	355.1
35	42.18	85	433.6
37[b]	47.07	90	527.8
40	55.32	95	633.0
45	71.88	100	760.0

[a] A more complete table is in Appendix C, Table 5. [b] Human body temperature.

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[10] If the water levels are not the same inside the flask and outside, a correction has to be calculated and applied to the room pressure to obtain the true pressure in the flask. For example, if the water level is higher inside the flask than outside, the pressure in the flask is lower than atmospheric pressure. The difference in levels is in millimeters of *water*, so this has to be converted to the equivalent in millimeters of mercury using the fact that the pressure exerted by a column of fluid is inversely proportional to the fluid's density.

Example 11.10
Collecting a Gas over Water

A sample of oxygen is collected over water at 15 °C and a pressure of 738 torr. Its volume is 316 mL. (a) What is the partial pressure, in torr, of the oxygen? (b) What would be its volume, in mL, at STP when the water is removed?

Analysis: There are two parts to this problem. Part (a) concerns the collection of a gas over water, and we will have to separate the partial pressure of oxygen from that of water. Part (b) of the question requires that we perform a gas law calculation to determine the volume at STP.

Assembling the Tools: For part (a) we will use Dalton's partial pressure equation,

$$P_{\text{total}} = P_{\text{water vapor}} + P_{O_2}$$

For part (b) we see that it will be most convenient to use the combined gas law.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

We might expect that we have to convert units as in previous problems. However, we note that R does not appear in any of our equations and we might not have to convert units; let's see.

Solution: Part (a): To calculate the partial pressure of the oxygen, we use Dalton's law. We will need the vapor pressure of water at 15 °C, which we find in Table 11.2 to be 12.8 torr. We rearrange the equation above to calculate P_{O_2}.

$$\begin{aligned} P_{O_2} &= P_{\text{total}} - P_{\text{water vapor}} \\ &= 738 \text{ torr} - 12.8 \text{ torr} = 725 \text{ torr} \end{aligned}$$

The answer to part (a) is that the partial pressure of O_2 is 725 torr.

Part (b): We'll begin by making a table of our data.

	Initial (1)			Final (2)	
P_1	725 torr	(which is P_{O_2})	P_2	760 torr	(standard pressure)
V_1	316 mL		V_2	the unknown is V_2	
T_1	288 K	(15.0 °C + 273)	T_2	273 K	(standard temperature)

We use these in the combined gas law equation; solving for V_2 and rearranging the equation a bit we have

$$V_2 = V_1 \times \left(\frac{P_1}{P_2}\right) \times \left(\frac{T_2}{T_1}\right)$$

Now we can substitute values and calculate V_2.

$$\begin{aligned} V_2 &= 316 \text{ mL} \times \left(\frac{725 \cancel{\text{torr}}}{760 \cancel{\text{torr}}}\right) \times \left(\frac{273 \cancel{\text{K}}}{288 \cancel{\text{K}}}\right) \\ &= 286 \text{ mL} \end{aligned}$$

Thus, when the water vapor is removed from the gas sample, the dry oxygen will occupy a volume of 286 mL at STP.

Are the Answers Reasonable? We know the pressure of the dry O_2 will be less than that of the wet gas, so the answer to part (a) seems reasonable. To check part (b), we can see if the pressure and temperature ratios move the volume in the correct direction. The pressure is increasing (720 torr ⟶ 760 torr), which should tend to lower the volume. The pressure ratio above will do that. The temperature change (293 K ⟶ 273 K) should also lower the volume, and once again, the temperature ratio above will have that effect. Our answer to part (b) is probably okay.

Practice Exercises

11.23 | A 2.50 L sample of methane was collected over water at 28 °C until the pressure in the flask was 775 torr. A small amount of $CaSO_4(s)$ was then added to the flask to absorb the water vapor (forming $CaSO_4 \cdot 2H_2O(s)$). What is the pressure inside the flask once all the water is absorbed? Assume that the addition of $CaSO_4(s)$ absorbed all the water and did not change the volume of the flask. How many moles of $CH_4(g)$ have been collected? (*Hint:* Find the partial pressure of water at 28 °C.)

11.24 | Suppose you prepared a sample of nitrogen and collected it over water at 15 °C at a total pressure of 745 torr and a volume of 317 mL. Find the partial pressure of the nitrogen, in torr, and the volume, in mL, it would occupy at STP.

Mole Fractions and Mole Percents

■ The concept of mole fraction applies to any uniform mixture in any physical state—gas, liquid, or solid.

One of the useful ways of describing the composition of a mixture is in terms of the *mole fractions* of the components. The **mole fraction** *is the ratio of the number of moles of a given component to the total number of moles of all components*. Expressed mathematically, the mole fraction of substance A in a mixture of $A, B, C, \ldots, Z$ substances is

TOOLS

Mole fractions

$$X_A = \frac{n_A}{n_A + n_B + n_C + n_D + \cdots + n_Z} \tag{11.4}$$

where X_A is the mole fraction of component A, and $n_A, n_B, n_C, \ldots, n_Z$ are the numbers of moles of each component, $A, B, C, \ldots, Z$, respectively. The sum of all mole fractions for a mixture must always equal 1.

You can see in Equation 11.4 that both numerator and denominator have the same units (moles), so they cancel. As a result, a mole fraction has no units. Nevertheless, always remember the definition: a mole fraction stands for the ratio of *moles* of one component to the total number of *moles* of all components.

Sometimes the mole fraction composition of a mixture is expressed on a percentage basis; we call it a **mole percent** (**mol%**). The mole percent is obtained by multiplying the mole fraction by 100 mol%.

Mole Fractions and Partial Pressures

Partial pressure data can be used to calculate the mole fractions of individual gases in a gas mixture because the number of *moles* of each gas is directly proportional to its partial pressure. We can demonstrate this as follows. The partial pressure, P_A, for any one gas, A, in a gas mixture with a total volume V at a temperature T is found by the ideal gas law equation, $PV = nRT$. So to calculate the number of moles of A present, we have

$$n_A = \frac{P_A V}{RT}$$

For any particular gas mixture at a given temperature, the values of V, R, and T are all constants, making the ratio V/RT a constant, too. We can therefore simplify the previous equation by using C to stand for V/RT. In other words, we can write

$$n_A = P_A C$$

The result is the same as saying that *the number of moles of a gas in a mixture of gases is directly proportional to the partial pressure of the gas.* The constant C is the same for all gases in the mixture. So by using different letters to identify individual gases, we can let $P_B C$ stand for n_B, $P_C\, C$ stand for n_C, and so on in Equation 11.4. Thus,

$$X_A = \frac{P_A C}{P_A C + P_B C + P_C C + \cdots + P_Z C}$$

The constant, C, can be factored out and canceled, so

$$X_A = \frac{P_A}{P_A + P_B + P_C + \cdots + P_Z}$$

The denominator is the sum of the partial pressures of all the gases in the mixture, but this sum equals the total pressure of the mixture (Dalton's law of partial pressures). Therefore, the previous equation simplifies to

$$X_A = \frac{P_A}{P_{\text{total}}} \tag{11.5}$$

Mole fraction related to partial pressure

Thus, the mole fraction of a gas in a gas mixture is simply the ratio of its partial pressure to the total pressure. Equation 11.5 also gives us a simple way to calculate the partial pressure of a gas in a gas mixture when we know its mole fraction.

Example 11.11
Using Mole Fractions to Calculate Partial Pressures

Suppose a mixture of oxygen and nitrogen is prepared in which there are 0.200 mol O_2 and 0.500 mol N_2. If the total pressure of the mixture is 745 torr, what are the partial pressures of the two gases in the mixture?

■ **Analysis:** This problem asks us to determine the partial pressures of two gases. We have seen a variety of equations so far; let's reason out which to use.

■ **Assembling the Tools:** The combined gas law cannot be used because it deals mainly with changing the P, V, and T conditions of a gas. We cannot solve the ideal gas law since two variables V and T are not given. Aside from the fact that we just discussed partial pressures and mole fractions, it seems that they are the logical choices. For this problem we use

$$X_{O_2} = \frac{\text{moles of } O_2}{\text{moles of } O_2 + \text{moles of } N_2} \quad \text{and} \quad X_{N_2} = \frac{\text{moles of } N_2}{\text{moles of } O_2 + \text{moles of } N_2}$$

and rearranging Equation 11.5 we get

$$P_{O_2} = X_{O_2} P_{\text{total}} \quad \text{and} \quad P_{N_2} = X_{N_2} P_{\text{total}}$$

■ **Solution:** The mole fractions are calculated as follows:

$$\begin{aligned} X_{O_2} &= \frac{\text{moles of } O_2}{\text{moles of } O_2 + \text{moles of } N_2} \\ &= \frac{0.200 \text{ mol}}{0.200 \text{ mol} + 0.500 \text{ mol}} \\ &= \frac{0.200 \text{ mol}}{0.700 \text{ mol}} = 0.286 \end{aligned}$$

Similarly, for N_2 we have[11]

$$X_{N_2} = \frac{0.500 \text{ mol}}{0.200 \text{ mol} + 0.500 \text{ mol}} = 0.714$$

---

[11] Notice that the sum of the mole fractions (0.286 + 0.714) equals 1.00. In fact, we could have obtained the mole fraction of nitrogen with less calculation by subtracting the mole fraction of oxygen from 1.00.

$$\begin{aligned} X_{O_2} + X_{N_2} &= 1.00 \\ X_{N_2} &= 1.00 - X_{O_2} \\ &= 1.00 - 0.286 = 0.714 \end{aligned}$$

We can now use Equation 11.5 to calculate the partial pressure. Solving the equation for partial pressure, we have

$$\begin{aligned} P_{O_2} &= X_{O_2} P_{\text{total}} \\ &= 0.286 \times 745 \text{ torr} \\ &= 213 \text{ torr} \end{aligned}$$

$$\begin{aligned} P_{N_2} &= X_{N_2} P_{\text{total}} \\ &= 0.714 \times 745 \text{ torr} \\ &= 532 \text{ torr} \end{aligned}$$

Thus, the partial pressure of O_2 is 213 torr and the partial pressure of N_2 is 532 torr.

■ **Is the Answer Reasonable?** There are three things we can check here. First, the mole fractions add up to 1.000, which they must. Second, the partial pressures add up to 745 torr, which equals the given total pressure. Third, the mole fraction of N_2 is somewhat more than twice that for O_2, so its partial pressure should be somewhat more than twice that of O_2. Examining the answers, we see this is true, so our answers should be correct.

Practice Exercises

11.25 | Sulfur dioxide and oxygen react according to the equation

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

If 50.0 g of $SO_2(g)$ is added to a flask resulting in a pressure of 0.750 atm, what will be the total pressure in the flask when a stoichiometric amount of oxygen is added? (*Hint:* This problem gives you more information than is needed.)

11.26 | Suppose a mixture containing 2.15 g H_2 and 34.0 g NO has a total pressure of 2.05 atm. What are the partial pressures of both gases in the mixture?

11.27 | What are the mole fraction and the mole percent of oxygen in exhaled air if P_{O_2} is 116 torr and P_{total} is 788 torr?

Graham's Law of Effusion

If you've ever walked past a restaurant and found your mouth watering after smelling the aroma of food, you've learned firsthand about diffusion! **Diffusion** is the spontaneous intermingling of the molecules of one gas, like those of the food aromas, with molecules of another gas, like the air outside the restaurant. (See Figure 11.12*a*). **Effusion**, on the other hand, is the gradual movement of gas molecules through a very tiny hole into a vacuum (Figure 11.12*b*). The rates at which both of these processes occur depends on the speeds of gas molecules; the faster the molecules move, the more rapidly diffusion and effusion occur.

The Scottish chemist Thomas Graham (1805–1869) studied the rates of diffusion and effusion of a variety of gases through porous clay pots and through small apertures. Comparing different gases at the same temperature and pressure, Graham found that their rates of effusion were inversely proportional to the square roots of their densities. This relationship is now called **Graham's law**.

$$\text{Effusion rate} \propto \frac{1}{\sqrt{d}} \qquad \begin{pmatrix}\text{when compared at the} \\ \text{same } T \text{ and } P\end{pmatrix}$$

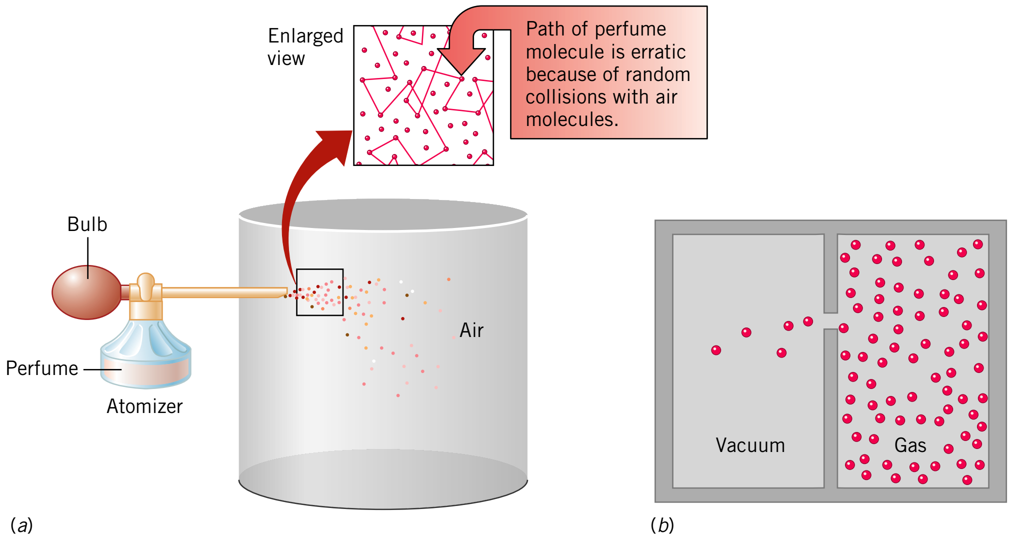
Enlarged view
Path of perfume molecule is erratic because of random collisions with air molecules.
Bulb
Perfume
Atomizer
Air
(a)
Vacuum
Gas
(b)

Figure 11.12 | **Spontaneous movements of gases.**
(*a*) Diffusion. (*b*) Effusion.

Graham's law is usually used to compare the rates of effusion of different gases, so the proportionality constant can be eliminated and an equation can be formed by writing the ratio of effusion rates:

■ By taking the ratio, the proportionality constant cancels from numerator and denominator.

$$\frac{\text{effusion rate }(A)}{\text{effusion rate }(B)} = \frac{\sqrt{d_B}}{\sqrt{d_A}} = \sqrt{\frac{d_B}{d_A}} \qquad (11.6)$$

CHEMISTRY AND CURRENT AFFAIRS | 11.2

Effusion and Nuclear Energy

The fuel used in almost all nuclear reactors is uranium, but only one of its naturally occurring isotopes, ^{235}U, can be easily split to yield energy. Unfortunately, this isotope is present in a very low concentration (about 0.72%) in naturally occurring uranium. Most of the element as it is mined consists of the more abundant isotope ^{238}U. Therefore, before uranium can be fabricated into fuel elements, it must be enriched to a ^{235}U concentration of about 2 to 5 percent. Enrichment requires that the isotopes be separated, at least to some degree.

Separating the uranium isotopes is not feasible by chemical means because the chemical properties of both isotopes are essentially identical. Instead, a method is required that is based on the very small difference in the masses of the isotopes. As it happens, uranium forms a compound with fluorine, UF_6, that is easily vaporized at a relatively low temperature. The UF_6 gas thus formed consists of two kinds of molecules, $^{235}UF_6$ and $^{238}UF_6$, with molecular masses of 349 and 352, respectively. Because of their different masses, their rates of effusion are slightly different; $^{235}UF_6$ effuses 1.0043 times faster than $^{238}UF_6$. Although the difference is small, it is sufficient to enable enrichment, provided the effusion is carried out over and over again enough times. In fact, it takes over 1400 separate effusion chambers arranged one after another to achieve the necessary level of enrichment.

Modern enrichment plants separate the $^{235}UF_6$ and $^{238}UF_6$ in a process using gas centrifuges. Inside the centrifuge the gases rotate at high speeds imparted by an impeller. The heavier $^{238}UF_6$ concentrates slightly toward the outer part of the centrifuge while the lighter $^{235}UF_6$ has slightly higher concentrations toward the center as shown in Figure 1. These are continuously separated, and repeated centrifugation steps lead to the desired purity.

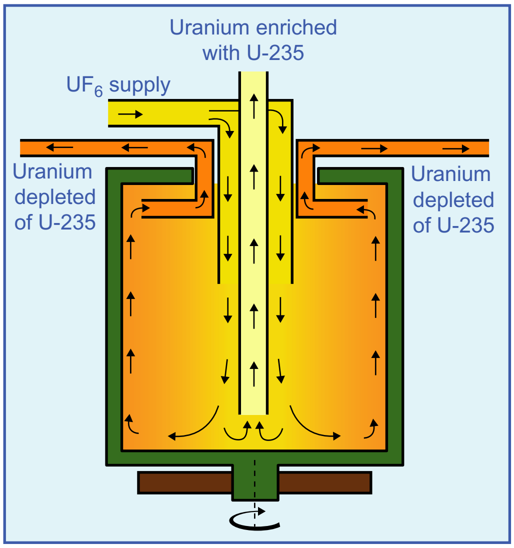
Uranium enriched with U-235
UF_6 supply
Uranium depleted of U-235
Uranium depleted of U-235

Figure 1 Isotopic Separation by Centrifugation
(Courtesy of Informationkreis KernEnergie, Berlin)

Earlier you saw that the density of a gas is directly proportional to its molar mass. Therefore, we can re-express Equation 11.6 as follows:

TOOLS

Graham's law of effusion

$$\frac{\text{effusion rate }(A)}{\text{effusion rate }(B)} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}} \tag{11.7}$$

where M_A and M_B are the molar masses of gases A and B.

Molecular masses also affect the rates at which gases undergo diffusion. Gases with low molar masses diffuse (and effuse) more rapidly than gases with high molar masses. Thus, hydrogen with a molar mass of 2 will diffuse more rapidly than methane, CH_4, with a molar mass of 16.

Example 11.12
Using Graham's Law

At a given temperature and pressure, which effuses more rapidly and by what factor: ammonia or hydrogen chloride?

■ **Analysis:** This is obviously a gas effusion problem that will require the use of Graham's law. Determining which effuses more rapidly, and obtaining a factor to describe how much more rapidly one effuses compared to the other will require that we set up the correct ratio of effusion rates.

■ **Assembling the Tools:** We are going to need Graham's law of effusion (Equation 11.7), which we can write as

$$\frac{\text{effusion rate }(\mathrm{NH_3})}{\text{effusion rate }(\mathrm{HCl})} = \sqrt{\frac{M_{\mathrm{HCl}}}{M_{\mathrm{NH_3}}}}$$

We will also recall how to calculate the molar masses of these two molecules.

■ **Solution:** The molar masses are 17.03 g/mol for NH_3 and 36.46 g/mol for HCl, so we immediately know that NH_3, with its smaller molar mass, effuses more rapidly than HCl. The ratio of the effusion rates is given by

$$\begin{aligned}\frac{\text{effusion rate }(\mathrm{NH_3})}{\text{effusion rate }(\mathrm{HCl})} &= \sqrt{\frac{M_{\mathrm{HCl}}}{M_{\mathrm{NH_3}}}}\\ &= \sqrt{\frac{36.46}{17.03}} = 1.463\end{aligned}$$

We can rearrange the result as

$$\text{effusion rate }(\mathrm{NH_3}) = 1.463 \times \text{effusion rate }(\mathrm{HCl})$$

Thus, ammonia effuses 1.463 times more rapidly than HCl under the same conditions.

■ **Is the Answer Reasonable?** The only quick check is to be sure that the arithmetic confirms that ammonia, with its lower molar mass, effuses more rapidly than the HCl, and that's what our result tells us.

Practice Exercises

11.28 | Bromine has two isotopes with masses of 78.9 and 80.9 (to three significant figures), respectively. Bromine boils at 59 °C. At 75 °C, what is the expected ratio of the rate of effusion of Br-81 compared to Br-79? (*Hint:* Recall that bromine is diatomic.)

11.29 | The hydrogen halide gases all have the same general formula, H*X*, where *X* can be F, Cl, Br, or I. If HCl(*g*) effuses 1.88 times more rapidly than one of the others, which hydrogen halide is the other: HF, HBr, or HI?

Analyzing and Solving Multi-Concept Problems

A long time ago, in a poorly equipped lab that had only a balance and an oven, a chemist was asked to determine the formula for a substance that by its crystalline nature appeared to be a single pure substance. The first thing he did was to take a sample of this unknown compound, with a mass of 2.121 g, and heat it at 250 °C for six hours. When cooled, the mass of the substance was now 1.020 g. While waiting for the sample to dry, the chemist tested the substance's solubility and found it was insoluble in water but did dissolve with the release of a gas when a strong acid was added. With that knowledge the chemist set up an apparatus to react the dry sample with acid and collect the gas evolved by bubbling it through water into a 265 mL collection flask. At that time the temperature was 24 °C and the atmospheric pressure was 738 torr and the gas completely filled the flask. Finally, the chemist weighed the flask with the gas and found it to be 182.503 g. The flask weighed 182.346 g when it contained only air. What is the formula for this compound?

Analysis To write a formula we need the elements that make up the compound and the molar ratio of the elements to each other. We are far from that point. Starting at the beginning, the weight loss on heating could be due to a wet sample or loss of water of hydration. If we knew how many moles of compound were in the remaining 1.020 g of sample, we could calculate the waters of hydration. The next experiment generated a gas that was carefully collected. It appears that we have all of the information—namely, *P*, *V*, and *T* to calculate the moles of gas. Knowing the masses of the flask with air and then with our compound allows us to calculate the mass of our sample and then its molar mass. In Chapter 5, Table 5.2, we've have a list of gases that can be generated by reaction of a substance with acid. Their molar masses are quite different from each other so we should be able to identify the gas. Once the identity of the gas is known, we can determine the molar mass of the possible cations. Once the cation is identified, we can return to the beginning and determine the number of water molecules in the hydrate.

Strategy Let's summarize our plan, keeping in mind that we do not have to use the data in the sequence presented. First, determine the moles of gas produced when the dry compound is dissolved in acid. Next, determine the molar mass of the gas and its identity and also the anion that produced it. Then, assuming that the cation could be either M^{+}, M^{2+}, or M^{3+}, we use the mole ratio with the anion and determine the atomic mass of the cation. We identify the cation if possible. Finally, we determine the number of water molecules in the hydrate and complete the chemical formula.

PART 1

Assembling the Tools We will need to correct the wet gas pressure for the vapor pressure of water.

$$P_{\text{dry}} = P_{\text{total}} - P_{\text{water}}$$

Next, we need to solve the ideal gas law for the moles of gas.

$$n = \frac{P\,V}{R\,T}$$

Finally, the molar mass is

$$\text{molar mass} = \frac{\text{mass of gas}}{\text{moles of gas}}$$

Solution The tabulated data in Appendix C. 5 tell us that the vapor pressure of water at 24 °C is 22.4 torr and therefore our pressure of the dry gas is 738 torr − 24 torr = 714 torr. Converting torr to atmospheres, we get 0.939 atm. We convert the volume to 0.265 L, and the temperature in kelvins is 297 K. Calculating *n* gives us

$$n = \frac{(0.939\ \cancel{\text{atm}})\,(0.265\ \cancel{\text{L}})}{(0.0821\ \cancel{\text{L}}\ \ \cancel{\text{atm}}\ \ \text{mol}^{-1}\ \ \cancel{\text{K}^{-1}})\,(297\ \cancel{\text{K}})} = 0.0102 \text{ moles}$$

PART 2

Assembling the Tools We need to calculate the mass of air inside the flask so we can get a mass with absolutely nothing inside the flask. Then we subtract the mass of the totally empty flask from the flask with our compound in it. The basic equation is the ideal gas law rearranged to calculate mass,

$$\text{mass} = \frac{P\,V \times \text{molar mass}}{R\,T}$$

Solution In Practice Exercise 11.13 it was stated that the average molar mass of air is 28.56 g mol^{-1}. Then the mass of the air in the flask is

$$\text{mass of air} = \frac{(0.939\ \cancel{\text{atm}})\,(0.265\ \cancel{\text{L}})\,(28.56\ \text{g}\ \cancel{\text{mol}^{-1}})}{(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})\,(297\ \cancel{\text{K}})} = 0.291\ \text{g air}$$

The mass of the totally empty flask is

$$182.346\ \text{g} - 0.291\ \text{g} = 182.055\ \text{g}$$

The mass of the unknown gas is then

$$182.503 - 182.055 = 0.448\ \text{g}$$

Dividing the mass of the unknown gas by the number of moles from Part 1 yields the molar mass,

$$\text{molar mass} = \frac{0.448\ \text{g gas}}{0.01020\ \text{moles gas}} = 43.9\ \text{g mol}^{-1}$$

Reviewing the gases in Table 5.2, we find that CO_2 is the only gas that has a molar mass close to 43.9 g mol^{-1}. We also know that CO_2 is released when carbonates are treated with acid. Therefore, the anion must be CO_3^{2-}.

PART 3

Assembling the Tools The tools in Chapter 4 show how to use mole ratios from the formulas M_2CO_3, MCO_3, and $M_2(CO_3)_3$ to calculate the moles of the cation. The same stoichiometry tools let us calculate the mass of the 0.102 moles of CO_3^{2-} in our compound. Subtracting the mass of carbonate from the mass of the sample gives us the mass of the cation.

As in Part 2, dividing the mass by the moles will give us the molar mass of the cation.

Solution The moles of cation in our 0.102-mole sample will depend on the charge of the anion. If the cation is M^+:

$$\text{moles of } M^+ = 0.0102\ \text{mol}\ CO_3^{2-} \times \frac{2\ \text{mol}\ M^+}{1\ \text{mol}\ CO_3^{2-}} = 0.0204\ \text{moles of } M^+$$

If the cation is M^{2+}:

$$\text{moles of } M^{2+} = 0.0102\ \text{mol}\ CO_3^{2-} \times \frac{1\ \text{mol}\ M^{2+}}{1\ \text{mol}\ CO_3^{2-}} = 0.0102\ \text{moles of } M^{2+}$$

If the cation is M^{3+}:

$$\text{moles of } M^{3+} = 0.0102\ \text{mol}\ CO_3^{2-} \times \frac{2\ \text{mol}\ M^{3+}}{3\ \text{mol}\ CO_3^{2-}} = 0.00680\ \text{moles of } M^{3+}$$

We have 0.0102 moles of CO_3^{2-} ions and the mass of carbonate is

$$0.0102 \text{ moles of } CO_3^{2-} \times \frac{60.0 \text{ g } CO_3^{2-}}{1 \text{ mol } CO_3^{2-}} = 0.612 \text{ g } CO_3^{2-}$$

Subtracting this from the 1.020 g sample, we have 0.408 g of cation.

Finally, dividing 0.408 g by the moles of each cation gives us the molar masses of the possible cations. We calculate

$$M^{+} = \frac{0.408 \text{ g M}}{0.0204 \text{ mol M}} = 20.0 \text{ g mol}^{-1}$$

$$M^{2+} = \frac{0.408 \text{ g M}}{0.0102 \text{ mol M}} = 40.0 \text{ g mol}^{-1}$$

$$M^{3+} = \frac{0.408 \text{ g M}}{0.0680 \text{ mol M}} = 60.0 \text{ g mol}^{-1}$$

Consulting the periodic table, we find that calcium with an atomic mass of 40 is the closest of all possibilities. Sodium, a +1 ion, has an atomic mass of 23 that is close to the calculated 20. However, our compound is insoluble and we know that sodium compounds are generally soluble, as shown in Table 5.1 on page 176. Therefore, our compound appears to be $CaCO_3$.

PART 4

Assembling the Tools The last step is to determine the number of water molecules in the hydrate. We have another stoichiometry step in which we calculate the moles of water per mole of compound. We already know the moles of compound, and this step simply involves converting the mass loss, which is water, to moles of water using the stoichiometry concepts in Chapter 4:

$$\text{moles } H_2O = \frac{\text{g } H_2O}{\text{molar mass } H_2O}$$

Solution The mass of water is the difference between the original mass and the dried mass.

$$\text{moles } H_2O = \frac{(2.121 \text{ g} - 1.020 \text{ g}) \ H_2O}{18.0 \text{ g } H_2O \text{ mol}^{-1}} = 0.0611 \text{ mol } H_2O$$

$$\text{moles } H_2O \text{ in hydrate} = \frac{\text{mol } H_2O}{\text{mol } CaCO_3} = \frac{0.0611 \text{ mol } H_2O}{0.0102 \text{ mol } CaCO_3} = 5.99 \text{ mol } H_2O$$

This properly rounds to 6 moles of water, and we then write $CaCO_3 \cdot 6H_2O$ as the final answer.

Are the Answers Reasonable? First, we recheck all of our calculations to be sure that all units cancel and that the math is correctly done. Finally, the fact that all the calculations result so precisely in a formula, $CaCO_3 \cdot 6H_2O$, with a whole number of waters of hydration, is a strong indication that the problem was solved correctly.

11.7 | Kinetic Molecular Theory

Scientists in the nineteenth century, who already knew the gas laws, wondered what had to be true, at the molecular level, about all gases to account for their conformity to a common set of gas laws. The **kinetic molecular theory of gases** provided an answer. We introduced some of its ideas in Chapter 7, and in Section 11.1 we described a number of observations that suggest what gases must be like when viewed at the molecular level. Let's look more closely now at the kinetic molecular theory to see how well it explains the behavior of gases.

The theory, often called simply the kinetic theory of gases, consisted of a set of postulates that describe the makeup of an ideal gas. Then the laws of physics and statistics were applied to see whether the observed gas laws could be predicted from the model. The results were splendidly successful.

■ The particles are assumed to be so small that they have no dimensions at all. They are essentially points in space.

Postulates of the Kinetic Theory of Gases

1. A gas consists of an extremely large number of very tiny particles that are in constant, random motion.
2. The gas particles themselves occupy a net volume so small in relation to the volume of their container that their contribution to the total volume can be ignored.
3. The particles often collide in perfectly elastic collisions[12] with themselves and with the walls of the container, and they move in straight lines between collisions, neither attracting nor repelling each other.

In summary, the model pictures an ideal gas as a collection of very small, constantly moving billiard balls that continually bounce off each other and the walls of their container, and so exert a net pressure on the walls (as described in Figure 11.1, page 474). The gas particles are assumed to be so small that their individual volumes can be ignored, so an ideal gas is effectively all empty space.

Kinetic Theory and the Gas Laws

According to the model, gases are mostly empty space. As we noted earlier, this explains why gases, unlike liquids and solids, can be compressed so much (squeezed to smaller volumes). It also explains why we have gas laws for gases, and *the same laws for all gases*, but not comparable laws for liquids or solids. The chemical identity of the gas does not matter, because gas molecules do not touch each other except when they collide, and there are extremely weak interactions, if any, between them.

We cannot go over the mathematical details, but we can describe some of the ways in which the laws of physics and the model of an ideal gas account for the gas laws and other properties of matter.

Definition of Temperature

The greatest triumph of the kinetic theory came with its explanation of gas temperature, which we discussed in Section 7.2. What the calculations showed was that the product of gas pressure and volume, PV, is proportional to the average kinetic energy of the gas molecules.

$$PV \propto \text{average molecular KE}$$

But from the experimental study of gases, culminating in the equation of state for an ideal gas, we have another term to which PV is proportional—namely, the Kelvin temperature of the gas.

$$PV \propto T$$

(We know what the proportionality constant here is—namely, nR—because by the ideal gas law, PV equals nRT.) With PV proportional *both* to T and to the "average molecular KE," then it must be true that the temperature of a gas is proportional to the average molecular KE.

$$T \propto \text{average molecular KE} \tag{11.8}$$

Boyle's Law

Using the model of an ideal gas, physicists were able to demonstrate that gas pressure is the net effect of innumerable collisions made by gas particles with the walls of the container. Let's imagine that one wall of a gas container is a movable piston that we can push in (or pull out) and so change the volume (see Figure 11.13). If we reduce the volume by one-half, we double the number of molecules per unit volume. This would double the number of collisions per second with each unit area of the wall and therefore double the pressure. Thus, cutting the volume in half forces the pressure to double, which is exactly what Boyle discovered:

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[12] In *perfectly elastic* collisions, no energy is lost by friction as the colliding objects deform momentarily.

$$P \propto \frac{1}{V} \qquad \text{or} \qquad V \propto \frac{1}{P}$$

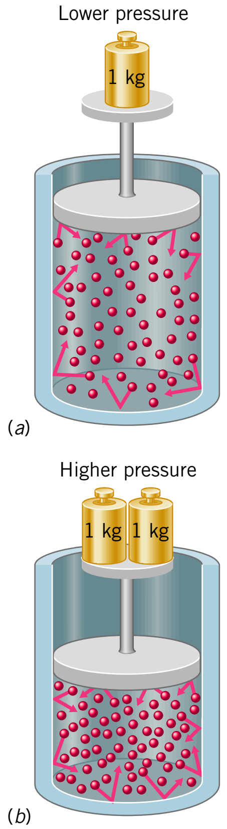

Figure 11.13 | **The kinetic theory and the pressure–volume law (Boyle's law).** When the gas volume is made smaller in going from (*a*) to (*b*), the number of collisions per second with each unit area of the container's walls increases. Therefore, the pressure increases.

Gay-Lussac's Law

As you learned earlier, the kinetic theory tells us that increasing the temperature increases the average velocity of gas particles. At higher velocities, the particles strike the container's walls more frequently and with greater force. If we don't change the volume, the *area* being struck remains the same, so the force per unit area (the pressure) must increase. Thus, the kinetic theory explains how the pressure of a fixed amount of gas is proportional to temperature (at constant volume), which is the pressure–temperature law of Gay-Lussac.

Charles' Law

We've just seen that the kinetic theory predicts that increasing the temperature should increase the pressure if the volume doesn't change. But suppose we wanted to keep the pressure constant when we raised the temperature. We could only do this if the volume of the container expanded (and therefore the surface area of the container walls increased) as the temperature increased. Therefore, a gas expands with increasing T in order to keep P constant, which is another way of saying that V is proportional to T at constant P. Thus, the kinetic theory explains Charles' law.

Dalton's Law of Partial Pressures

The law of partial pressures is actually evidence for that part of the third postulate in the kinetic theory that pictures particles of an ideal gas moving in straight lines between collisions, neither attracting nor repelling each other (see Figure 11.14). By not interacting with each other, the molecules act *independently,* so each gas behaves as though it were alone in the container. Only if the particles of each gas do act independently can the partial pressures of the gases add up in a simple way to give the total pressure.

Graham's Law of Effusion

The key conditions of Graham's law are that the rates of effusion of two gases with different molecular masses must be compared at the same pressure and temperature and under conditions where the gas molecules do not hinder each other. When two gases have the same temperature, their particles have identical average molecular kinetic energies. Using subscripts 1 and 2 to identify two gases with molecules having different masses m_1 and m_2, we can write that at a given temperature,

$$\overline{KE}_1 = \overline{KE}_2$$

where the bar over KE signifies "average."

For a single molecule, its kinetic energy is $KE = \frac{1}{2}mv^2$. For a large collection of molecules of the same substance, the average kinetic energy is $\overline{KE} = \frac{1}{2}m\overline{v^2}$, where $\overline{v^2}$ is the *average of the velocities squared* (called the *mean square* velocity). We have not extended the "average" notation (the bar) over the mass because all the molecules of a given substance have the same mass (the average of their masses is just the mass).

Once again comparing two gases, 1 and 2, we take $\overline{v_1^2}$ and $\overline{v_2^2}$ to be the average of the velocities squared of their molecules. If both gases are at the same temperature, we have

$$\overline{KE}_1 = \frac{1}{2}m_1\overline{v_1^2} = \frac{1}{2}m_2\overline{v_2^2} = \overline{KE}_2$$

Now let's rearrange the previous equation to get the ratio of $\overline{v^2}$ terms.

$$\frac{\overline{v_1^{\,2}}}{\overline{v_2^{\,2}}} = \frac{m_2}{m_1}$$

Next, we'll take the square root of both sides. When we do this, we obtain a ratio of quantities called the **root mean square** (abbreviated **rms**) **speeds**, which we will represent as $(\overline{v_1})_{\text{rms}}$ and $(\overline{v_2})_{\text{rms}}$.

$$\frac{(\overline{v_1})_{\text{rms}}}{(\overline{v_2})_{\text{rms}}} = \sqrt{\frac{m_2}{m_1}}$$

■ Suppose we have two molecules with speeds of 6 and 10 m s^{-1}. The average speed is $\frac{1}{2}(6 + 10) = 8$ m s^{-1}. The rms speed is obtained by squaring each speed, averaging the squared values, and then taking the square root of the result. Thus,

$$\overline{v_{\text{rms}}} = \sqrt{\frac{1}{2}(6^2 + 10^2)} = 8.2 \text{ m s}^{-1}$$

The rms speed, $\overline{v_{\text{rms}}}$, is not actually the same as the average speed of the gas molecules, but instead represents the speed of a molecule that would have the average kinetic energy. (The difference is subtle, and the two averages do not differ by much, as noted in the margin.)

For any substance, the mass of an individual molecule is proportional to the molar mass. Representing a molar mass of a gas by M, we can restate this as $m \propto M$. The proportionality constant is the same for all gases. (It's in grams per atomic mass unit when we express m in atomic mass units.) When we take a ratio of two molar masses, the constant cancels anyway, so we can write

$$\frac{(\overline{v_1})_{\text{rms}}}{(\overline{v_2})_{\text{rms}}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}}$$

According to the preceding equation, the rms speed of the molecules is inversely proportional to the square root of the molecular mass. This means that *at a given temperature, molecules of a gas with a high molecular mass move more slowly, on average, than molecules of a gas with a low molecular mass.*

As you might expect, fast-moving molecules will find an opening in the wall of a container more often than slow-moving molecules, so they will effuse faster. Therefore, the rate of effusion of a gas is proportional to the average speed of its molecules, and therefore, it is also proportional to $1/\sqrt{M}$.

$$\text{Effusion rate} \propto \overline{v_{\text{rms}}} \propto \frac{1}{\sqrt{M}}$$

Let's use k as the proportionality constant. This gives

$$\text{effusion rate} = \frac{k}{\sqrt{M}}$$

Comparing two gases, 1 and 2, and taking a ratio of effusion rates to cause k to cancel, we have

$$\frac{\text{effusion rate (gas 1)}}{\text{effusion rate (gas 2)}} = \sqrt{\frac{M_2}{M_1}}$$

This is the way we expressed Graham's law in Equation 11.7. Thus, still another gas law supports the model of an ideal gas.

Absolute Zero Defined

The kinetic theory found that the temperature is proportional to the average kinetic energy of the molecules.

$$T \propto \text{average molecular } KE \propto \frac{1}{2}m\overline{v^2}$$

If the average molecular KE becomes zero, the temperature must also become zero. However, mass (m) cannot become zero, so the only way that the average molecular KE

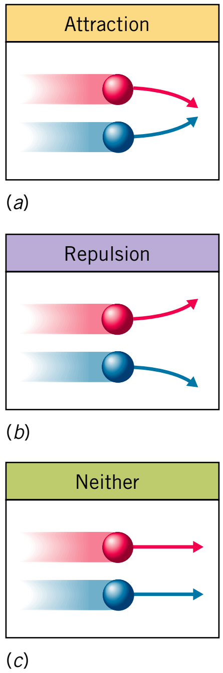

Figure 11.14 | **Gas molecules act independently when they neither attract nor repel each other.** Gas molecules would not travel in straight lines if they attracted each other as in (*a*) or repelled each other as in (*b*). They would have to travel farther between collisions with the walls and, therefore, would collide with the walls less frequently. This would affect the pressure. Only if the molecules traveled in straight lines with no attractions or repulsions, as in (*c*), would their individual pressures not be influenced by near misses or by collisions between the molecules.

can be zero is if v goes to zero. A particle cannot move any slower than it does at a dead standstill, so if the particles stop moving entirely, the substance is as cold as anything can get. It's at absolute zero.[13]

11.8 | Real Gases

According to the ideal gas law, the ratio PV/T for a given gas sample equals a product of two constants, nR. Experimentally, however, for real gases PV/T is actually not quite a constant. When we use experimental values of P, V, and T for a real gas, such as O_2, to plot actual values of PV/T as a function of P, we get the curve shown in Figure 11.15. The *horizontal* line at $PV/T = 1$ in Figure 11.15 is what we should see if PV/T were truly constant over all values of P, as it would be for an ideal gas.

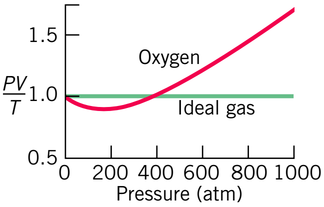

Figure 11.15 | **Deviation from the ideal gas law.** A graph of PV/T versus P for an ideal gas is a straight line, as shown. The same plot for oxygen, a real gas, is not a straight line, showing that O_2 is not "ideal."

A real gas, like oxygen, deviates from ideal behavior for two important reasons. First, in an ideal gas there would be no attractions between molecules, but in a real gas molecules do experience weak attractions toward each other. Second, the model of an ideal gas assumes that gas molecules are infinitesimally small—that the individual molecules have no volume. But real molecules do take up some space. (If all of the kinetic motions of the gas molecules ceased and the molecules settled, you could imagine the net space that the molecules would occupy in and of themselves.)

At room temperature and atmospheric pressure, most gases behave nearly like an ideal gas, also for two reasons. First, the molecules are moving so rapidly and are so far apart that the attractions between them are hardly felt. As a result, the gas behaves almost as though there are no attractions. Second, the space between the molecules is so large that the volume occupied by the molecules themselves is insignificant. By doubling the pressure, we are able to squeeze the gas into very nearly half the volume.

Let's examine Figure 11.15 more closely. Starting at low pressures, close to $P = 1$, gases often behave as ideal gases. As the pressure is increased along the x-axis, the gas particles must be closer together. The first effect noticed as gas particles get closer are attractive forces. These forces between molecules reveal themselves by causing the pressure of a real gas to be slightly lower than that expected for an ideal gas. The attractions cause the paths of the molecules to bend whenever they pass near each other (Figure 11.16). Because the molecules are not traveling in straight lines, as they would in an ideal gas, they have to travel farther between collisions with the walls. As a result, the molecules of a real gas don't strike the walls as frequently as they would if the gas were ideal, and this reduced frequency of collision translates to a reduced pressure. Thus, the ratio PV/T is *less* than that for an ideal gas. The curve for O_2 in Figure 11.15, therefore, dips when we are just starting to increase the pressure.

As we increase the pressure further, the fact that gas molecules must occupy some space becomes more important than the attractive forces. Continued increases in pressure can reduce only the empty space between the molecules, not the volume of the individual particles themselves. So, at very high pressure, the space occupied by the molecules themselves is a significant part of the total volume, and doubling the pressure cannot halve the total volume. As a result, the actual volume of a real gas is larger than expected for an ideal gas, and the ratio PV/T becomes larger as the pressure increases. We see this for O_2 at the right side of the graph in Figure 11.15.

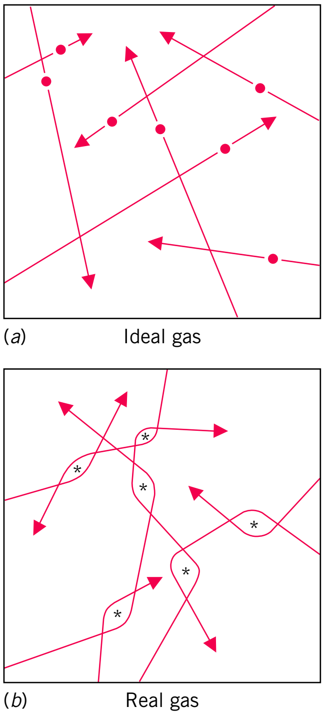

Figure 11.16 | **The effect of attractive forces on the pressure of a real gas.** (*a*) In an ideal gas, the molecules travel in straight lines. (*b*) In a real gas, the paths curve as one molecule passes close to another because the molecules attract each other. Asterisks indicate the points at which molecules come close to each other.

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[13] Actually, even at 0 K, there must be some slight motion. It's required by the Heisenberg uncertainty principle, which says (in one form) that it's impossible to know precisely both the speed and the location of a particle simultaneously. (If one knows the speed, then there's uncertainty in the location, for example.) If the molecules were actually dead still at absolute zero, there would be no uncertainty in their speed—but then the uncertainty in their *position* would be infinitely great. We would not know where they were! But we do know; they're in this or that container. Thus some uncertainty in speed must exist to have less uncertainty in position and so locate the sample!

The van der Waals Equation

■ J. D. van der Waals (1837–1923), a Dutch scientist, won the 1910 Nobel Prize in physics.

Many attempts have been made to modify the equation of state of an ideal gas to get an equation that better fits the experimental data for individual real gases. One of the more successful efforts was that of J. D. van der Waals. He found ways to correct the measured values of P and V to give better fits of the data to the general gas law equation. The result of his derivation is called the *van der Waals equation of state for a real gas.* Let's take a brief look at how van der Waals made corrections to measured values of P and V to obtain expressions that fit the ideal gas law.

As you know, if a gas were ideal, it would obey the equation

$$P_{\text{ideal}}V_{\text{ideal}} = nRT$$

However, for a real gas, using the measured pressure, P_{meas}, and measured volume, V_{meas},

$$P_{\text{meas}}V_{\text{meas}} \neq nRT$$

The reason is because P_{meas} is smaller than P_{ideal} (as a result of attractive forces between real gas molecules), and because V_{meas} is larger than V_{ideal} (because real molecules do take up some space). Therefore, to get the pressure and volume to obey the ideal gas law, we have to *add* something to the measured pressure and *subtract* something from the measured volume. That's exactly what van der Waals did. Here's his equation.

TOOLS

van der Waals equation of state for real gases

$$\left(\overset{\substack{\text{The measured}\\ \text{pressure}\\ \downarrow}}{P_{\text{meas}}} + \underset{\substack{\nearrow\\ \text{Correction to bring}\\ \text{measured } P \text{ up to the}\\ \text{pressure an ideal gas}\\ \text{would exert}}}{\frac{n^2a}{V^2}}\right)\left(\overset{\substack{\text{The measured}\\ \text{volume}\\ \downarrow}}{V_{\text{meas}}} - \underset{\substack{\uparrow\\ \text{Correction to reduce}\\ \text{measured } V \text{ to the volume}\\ \text{an ideal gas would have}}}{nb}\right) = nRT \tag{11.9}$$

The constants a and b are called *van der Waals constants* (see Table 11.3). They are determined for each real gas by carefully measuring P, V, and T under varying conditions.

Table 11.3 van der Waals Constants

Substance	a (L^2 atm mol^{-2})	b (L mol^{-1})
Noble Gases		
Helium, He	0.03421	0.02370
Neon, Ne	0.2107	0.01709
Argon, Ar	1.345	0.03219
Krypton, Kr	2.318	0.03978
Xenon, Xe	4.194	0.05105
Other Gases		
Hydrogen, H_2	0.02444	0.02661
Oxygen, O_2	1.360	0.03183
Nitrogen, N_2	1.390	0.03913
Methane, CH_4	2.253	0.04278
Carbon dioxide, CO_2	3.592	0.04267
Ammonia, NH_3	4.170	0.03707
Water, H_2O	5.464	0.03049
Ethyl alcohol, C_2H_5OH	12.02	0.08407

Then trial calculations are made to figure out what values of the constants give the best matches between the observed data and the van der Waals equation.

Notice that the constant *a* involves a correction to the pressure term of the ideal gas law, so the size of *a* would indicate something about attractions between molecules. Larger values of *a* mean stronger attractive forces between molecules. Thus, the most easily liquefied substances, like water and ethyl alcohol, have the largest values of the van der Waals constant *a*, suggesting relatively strong attractive forces between their molecules.

The constant *b* helps to correct for the volume occupied by the molecules themselves, so the size of *b* indicates something about the sizes of particles in the gas. Larger values of *b* mean larger molecular sizes. Looking at data for the noble gases in Table 11.3, we see that as the atoms become larger from helium through xenon, the values of *b* become larger. In the next chapter we'll continue the study of factors that control the physical state of a substance, particularly attractive forces and their origins.

11.9 | Chemistry of the Atmosphere

The atmosphere of the earth is the layer of gases held close to the surface of the planet by gravitational forces. There is no distinct boundary between our atmosphere and outer space, but the concentration of atmospheric gases is greatest at the earth's surface and decreases steadily with altitude. Seventy five percent of the mass of the atmosphere exists below an altitude of 11 km and 99% is found below 30 km, yet spacecraft returning to earth start having frictional heating due to atmospheric molecules at an altitude of 120 km.

Our atmosphere is the only source of the oxygen we, and other animals, breathe and it is the repository for our exhaled carbon dioxide and water vapor. The carbon dioxide in our atmosphere is essential for plants that derive their energy from photosynthesis. Below we consider other chemical and physical properties of our atmosphere that are important to us as chemists and citizens.

Composition of the Atmosphere

Both the chemical composition and physical properties of the atmosphere vary with time and location. Some vary slightly, and others vary significantly from time to time and place to place.

On a dry basis (without water) the gases that surround us are a fairly constant mixture of nitrogen (78.08%), oxygen (20.95%), and argon (0.93%), and traces of other gases (0.04%). Carbon dioxide varies seasonally and by location but comprises almost all of the trace gases at about 0.038%. Water vapor can reach 4% of the atmospheric gases or it can be close to 0% depending on weather conditions. When water is factored in, the percentages of the other elements decrease proportionally. The concentration of ozone, O_3, is very small and varies by location and altitude.

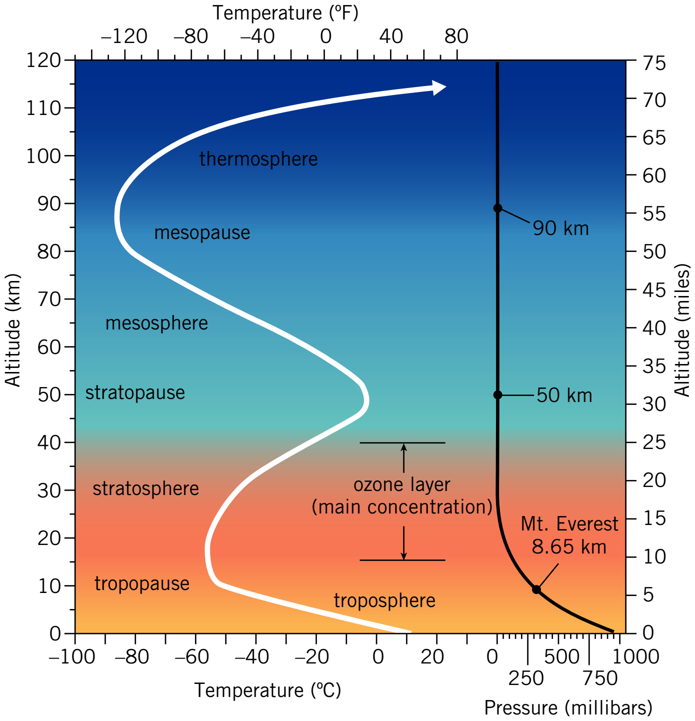

Figure 11.17 | **A representation of the Earth's atmosphere.** The white line represents the temperature and the black line represents the pressure.

In addition to the chemical composition, the physical properties of the atmosphere are important. Figure 11.17 illustrates the pressure and the temperature profile of the atmosphere. Whereas we can see that the pressure of atmospheric gases decreases logarithmically with altitude (a factor of 10 for each 17 km increase in altitude) in a regular manner, the temperature is another matter. Figure 11.17 illustrates that starting from the surface of the Earth, the temperature decreases to the top of the troposphere, then it increases through the stratosphere, approaching the temperature at the surface of the earth. In the mesosphere the temperature decreases again, and yet again it increases in the thermosphere.

We also notice from Figure 11.17 that the "ozone layer" exists at an altitude of approximately 27 km. Also, at higher altitudes, the lighter elements such as H_2 and He dominate the atmospheric composition.

Ozone and the Ozone Layer

Ozone, O_3, forms when molecular oxygen, O_2, is broken apart into oxygen atoms (Equation 11.10), and those atoms combine with O_2 (Equation 11.11).

$$O_2 + \text{energy} \longrightarrow 2O \tag{11.10}$$

$$O + O_2 \longrightarrow O_3 \tag{11.11}$$

■ Molecular oxygen provides life on earth with some protection from high energy radiation.

The energy for the first reaction comes from high-energy photons (with wavelengths less than 240 nm) from outer space. At the surface of the earth the energy comes from lightning, electrical sparks from motors, and other machinery and some chemical processes. Equation 11.11 shows the combination of atomic oxygen and molecular oxygen to form ozone.

Ozone is a very reactive form of oxygen, acting as an oxidizing agent. Ozone is used to purify water, similar to the way chlorine is used in most municipal water systems. The oxidizing strength of ozone is sufficient to kill most microorganisms. Ozone is also an irritant. Contact with mucus membranes in the eyes or respiratory tract often causes severe reactions that may require medical treatment. Ozone can react with the rubber in automobile tires causing premature failure. Ozone is also an important reactant in the formation of photochemical smog in major cities and the blue haze in wilderness areas. Aside from its use in purifying drinking water, ozone at low altitudes in the atmosphere is usually considered an unwanted pollutant.

On the other hand, the ozone layer that forms at an altitude of approximately 27 km above the earth's surface is considered to be essential and beneficial. The ozone layer is beneficial because ozone absorbs harmful ultraviolet radiation emitted by the sun in the reaction

$$O_3 + h\nu \longrightarrow O_2 + O \tag{11.12}$$

where $h\nu$ represents electromagnetic radiation in the range of 240–320 nm. As a result, harmful, cancer-causing, ultraviolet radiation is greatly reduced by the ozone layer before it reaches the surface of the earth.

■ A steady state differs from a dynamic equilibrium in that the formation reaction is different from the decomposition reaction.

■ CFC is an abbreviation for the word "chlorofluorocarbon," indicating organic compounds containing chlorine, fluorine, and carbon.

In normal situations, the ozone in the ozone layer is replenished by the formation reactions (Equations 11.10 and 11.11) as fast as it is depleted (Equation 11.12), resulting in a **steady-state** concentration of ozone. This steady state can be altered if other substances also destroy ozone at a significant rate. In the past 50 years many substances that destroy ozone have been identified, and most contain chlorine. Chlorine can enter the atmosphere in a variety of ways, from natural emissions from oceans or volcanoes that release HCl(*g*) to Freon-type refrigerants containing chlorine, called CFCs. There was concern that the amount of these ozone-destroying molecules would destroy enough ozone to be a serious worldwide health hazard. The *Montreal Protocol*, which bans CFCs, was signed on September 16, 1987.

About the same time, atmospheric scientists were realizing that the ozone layer over Antarctica was severely depleted each October (springtime in the Southern Hemisphere). Usually ozone levels would decrease in the total darkness of winter at the south pole and then increase as the sun began shining again. However, when the sun appeared, the ozone levels dropped dramatically, creating what was popularly called an "**ozone hole**." The puzzle was figured out when it was demonstrated that clouds of ice crystals containing reactive chlorine compounds melted in the spring, releasing these compounds. The chlorine compounds had been accumulating in the ice crystals all winter at temperatures as low as −80 °C. It is important to note that the ozone hole has no direct relationship to **global climate change**.

Greenhouse Gases and Global Temperature Change

It has been calculated that if the earth's atmosphere did not exist or did not trap heat energy, the average temperature would be −18 °C (0 °F). With our atmosphere trapping some heat energy, the average temperature is a toasty 14 °C. **Greenhouse gases** are those atmospheric gases that absorb energy and keep the Earth warm. We just don't want it to be too warm.

The operation of a greenhouse provides an imperfect, simplistic, but reasonable analogy for describing heat exchange on the Earth. To maintain an optimum temperature in a greenhouse, windows in the ceiling are opened to let excess heat energy escape at a rate that balances the incoming energy of the sun. This is another steady-state situation similar to the ozone layer. If one or more of the windows are closed the steady state will be disturbed and two things will happen. First, the temperature starts to rise and second, as the temperature rises, more heat energy will escape from the remaining open windows. At some point the temperature will rise enough so that the flow of energy into and out of the greenhouse will once again reach a steady state. The greenhouse will then be at a new, higher, temperature that will remain constant until another window is open or closed.

Now we consider the Earth. The major flows of energy are the energy reaching the Earth's surface from unreflected sunlight. Sunlight reflected from clouds, snow, and other surfaces does not appreciably contribute to the greenhouse effect. Sunlight absorbed by the plants, soil, oceans, and so on must be re-emitted to outer space. Figure 8.5 on page 311 illustrates how green plants absorb visible light.

■ Most of the energy of sunlight is in the ultraviolet and visible spectral regions.

Classical physics tells us that the re-emitted radiation occurs in the infrared region of the spectrum. Some gases, such as water, carbon dioxide, and methane in particular (the main greenhouse gases) absorb infrared radiation. Figure 8.4 on page 311 illustrates how compounds can absorb infrared energy. When a greenhouse gas absorbs infrared radiation it is analogous to closing some windows in our greenhouse. The higher the concentration of the gases, the more the windows, at particular wavelengths, are closed. The windows representing water and carbon dioxide are almost completely closed already. In this analogy the window for methane is still about half open. The result is that doubling the CO_2

ON THE CUTTING EDGE | **11.3**

Super Greenhouse Gases

Our common greenhouse gases are water, carbon dioxide, and methane. These are widely held to be responsible for the comfortable temperature of our planet and also the rise in temperature over the last century. A completely different set of gases, the chlorofluorocarbons, CFCs, were used as propellants in consumer sprays and air-conditioning systems. These compounds have been implicated in destroying ozone in the stratosphere. R. S. Mario Molina, Paul Crutzen, and F. Sherwood Rowland were awarded the 1995 Nobel Prize in chemistry[1] for explaining how the chlorine from CFCs finds its way to the South Pole to form the famous "ozone hole."

A new class of compounds, fluorinated hydrocarbons, HFCs, were developed to replace the CFCs that were destroying ozone. They are now commonly used as propellants and in air conditioners. The most common of these is 1,1-difluoroethane, or HFC-134a (Figure 1). It turns out that HFC-134a appears to be a "super greenhouse gas." This means that its effect on global climate may be much greater than water, carbon dioxide, and methane combined. Apparently one problem has been solved but another may have been created.

Some futurists, when considering that humans will some day overflow our home planet, have been looking for other sites for human habitation. In the early 2000s some asked if we could habitate Mars (Figure 2) if it were just a bit warmer. Since then, researchers have been investigating whether or not it would be feasible to use global warming to heat another globe—Mars. It seems to be possible; however, we are reminded by experience with HFCs that often solutions may cause their own problems.

Figure 1 Space-filling model of 1,1-difluoroethane.

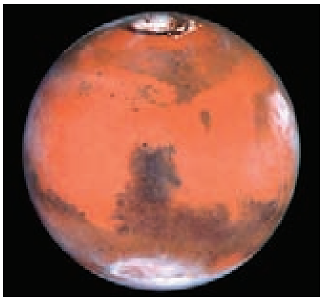

Figure 2 Mars—a candidate for artificial global warming?
NASA/JPL Photo

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[1] F. S. Rowland and M. J. Molina, "*Ozone Depletion: 20 Years after the Alarm,*" *Chemical and Engineering News* 72, 8–13, 1994.

in the atmosphere will cause a rise in the temperature, but doubling the concentration of methane will have a much greater effect. This occurs because the amount of open window that is available to be closed by methane is much more than the open window that can be closed by carbon dioxide. Atmospheric scientists call this idea "forcing." Methane has a greater temperature-forcing potential than carbon dioxide.

Overall, gases that absorb infrared radiation can be considered to be greenhouse gases. Global increases in the concentrations of those gases will lead to temperature increases. The physical consequences of global temperature change include crop and species dislocation. Weather changes and changes in ocean levels resulting in flooding are also predicted.

Summary

Barometers, Manometers, and Pressure Units. Atmospheric pressure is measured with a **barometer**, in which a pressure of one **standard atmosphere (1 atm)** will support a column of mercury 760 mm high. This is a pressure of 760 **torr**. By definition, 1 atm = 101,325 **pascals (Pa)** and 1 **bar** = 100 kPa. **Manometers**, both open-end and closed-end, are used to measure the pressure of trapped gases.

Gas Laws. An **ideal gas** is a hypothetical gas that obeys the gas laws exactly over all ranges of pressure and temperature. Real gases exhibit ideal gas behavior most closely at low pressures and high temperatures, which are conditions remote from those that liquefy a gas.

Boyle's Law (Pressure–Volume Law). For a fixed amount of gas at constant temperature, volume varies inversely with pressure. $V \propto 1/P$. A useful form of the equation is $P_1V_1 = P_2V_2$.

Charles' Law (Temperature–Volume Law). For a fixed amount of gas at constant pressure, volume varies directly with the Kelvin temperature. $V \propto T$, or $V_1/V_2 = T_1/T_2$.

Gay-Lussac's Law (Temperature–Pressure Law). For a fixed amount of gas at constant volume, pressure varies directly with Kelvin temperature. $P \propto T$, or $P_1/P_2 = T_1/T_2$.

Avogadro's Principle. Equal volumes of gases contain equal numbers of moles when compared at the same temperature and pressure. At **STP**, 273.15 K and 1.00 atm, 1 mol of an ideal gas occupies a volume of 22.4 L.

Combined Gas Law. PV divided by T for a given gas sample is a constant. $PV/T = C$, or $P_1V_1/T_1 = P_2V_2/T_2$.

Ideal Gas Law. $PV = nRT$. When P is in atm and V is in L, the value of R is 0.0821 L atm mol^{-1} K^{-1} (T is, as usual, in kelvins).

Gay Lussac's Law of Combining Volumes. When measured at the same temperature and pressure, the volumes of gases consumed and produced in chemical reactions are in the same ratios as their coefficients.

Mole Fraction. The mole fraction X_A of a substance A equals the ratio of the number of moles of A, n_A, to the total number of moles n_{total} of all the components of a mixture.

$$X_A = \frac{n_A}{n_{\text{total}}}$$

Dalton's Law of Partial Pressures. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

$$P_{\text{total}} = P_A + P_B + P_C + \cdots$$

In terms of mole fractions, $P_A = X_AP_{\text{total}}$ and $X_A = P_A/P_{\text{total}}$.

Graham's Law of Effusion. The rate of effusion of a gas varies inversely with the square root of its density (or the square root of its molecular mass) at constant pressure and temperature. Comparing different gases at the same temperature and pressure,

$$\frac{\text{effusion rate }(A)}{\text{effusion rate }(B)} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}$$

Kinetic Theory of Gases. An ideal gas consists of a large number of particles, each having essentially zero volume, that are in constant, chaotic, random motion, traveling in straight lines with no attractions or repulsions between them. When the laws of physics and statistics are applied to this model and the results compared with the ideal gas law, the Kelvin temperature of a gas is found to be proportional to the average kinetic energy of the gas particles. Pressure is the result of the force and frequency of collisions of the particles with the container's walls.

Real Gases. Because individual gas particles do have real volumes and because small forces of attraction do exist between them, real gases do not exactly obey the gas laws. The van der Waals equation of state for a real gas makes corrections for the volume of the gas molecules and for the attractive force between gas molecules. The van der Waals constant a provides a measure of the strengths of the attractive forces between molecules, whereas the constant b gives a measure of the relative size of the gas molecules.

Reaction Stoichiometry: A Summary. With the study in this chapter of the stoichiometry of reactions involving gases, we

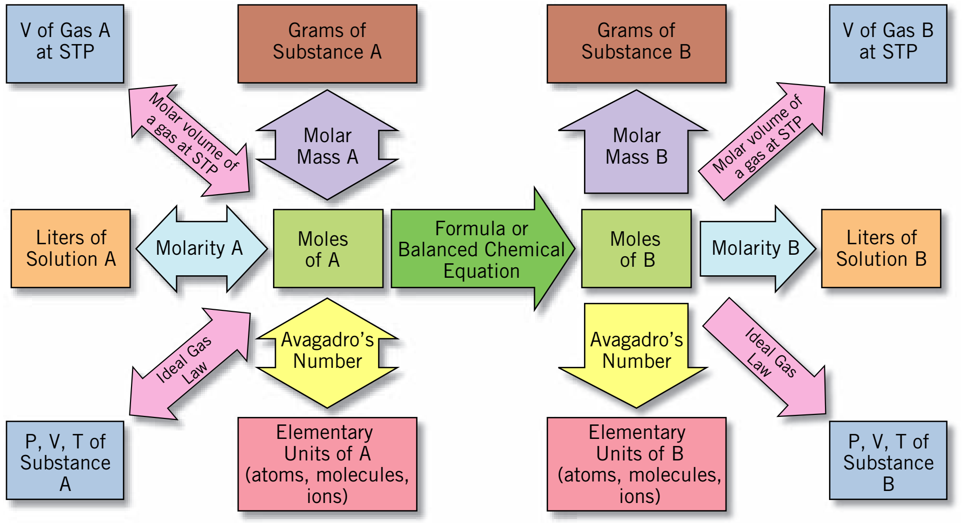

V of Gas A at STP
Grams of Substance A
Grams of Substance B
V of Gas B at STP
Molar volume of a gas at STP
Molar Mass A
Molar Mass B
Molar volume of a gas at STP
Liters of Solution A
Molarity A
Moles of A
Formula or Balanced Chemical Equation
Moles of B
Molarity B
Liters of Solution B
Ideal Gas Law
Avagadro's Number
Avagadro's Number
Ideal Gas Law
P, V, T of Substance A
Elementary Units of A (atoms, molecules, ions)
Elementary Units of B (atoms, molecules, ions)
P, V, T of Substance B

Figure 11.18 | **Pathways for working stoichiometry problems.** This diagram adds two additional ways to convert laboratory units to moles. As in Figures 4.6 and 5.27, the boxed items are given or calculated quantities while the arrows indicate where to find the conversion factors.

now have the tools needed for the calculations of all variations of reaction stoichiometry. The critical link in all such calculations is the set of coefficients given by the balanced chemical equation, which provides the stoichiometric equivalencies needed to convert from the number of moles of one substance into the numbers of moles of any of the others in the reaction. To use the coefficients requires that all the calculations must funnel through *moles.* Whether we start with grams of some compound in a reaction, or the molarity of its solution plus a volume, or *P-V-T* data for a gas in the reaction, *we must get the essential calculation into moles*. After applying the coefficients, we can then move back to any other kind of unit we wish. The flowchart in Figure 11.18 summarizes what we have been doing.

The labels on the arrows of the flowchart suggest the basic tools. Formula masses or molecular masses get us from grams to moles or from moles to grams. Molarity and volume data move us from concentration to moles or back. With *P-V-T* data we can find moles or, knowing moles of a gas, we can calculate *P, V,* or *T,* as long as the other two are known.

The Atmosphere: A Summary. In this section we have briefly learned about the structure and chemical composition of the atmosphere that gradually becomes less dense with increasing altitude. The **ozone layer** has a steady-state concentration that depends on the continuous formation and destruction of ozone molecules, O_3. Loss of ozone at the poles causes a situation called the "**ozone hole**." **Greenhouse gases**, H_2O, CO_2, and CH_4, naturally cause the earth to be warmer than it would be if they were not present. Excess amounts of CO_2 and CH_4 are of concern because of the potential for significant **global climate changes**.

TOOLS

Tools for Problem Solving

Below we list the tools you have learned in this chapter. Most of these are mathematical relationships. Review all these tools and refer to them, if necessary, when working on the Review Questions and Problems that follow.

Combined gas law (page 483)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This law applies when the amount of gas is constant and we are asked how one of the variables (*P, V,* or *T*) changes when we change two of the others. When the amount of gas and one of the variables (*P, V,* or *T*) are constant, the problem reduces to one involving Boyle's, Charles', or Gay-Lussac's law.

Ideal gas law (page 491)

$$PV = nRT$$

This law applies when any three of the four variables P, V, T, or n, are known and we wish to calculate the value of the fourth.

Determination of molar mass:

from the ideal gas law (page 493),

$$\text{molar mass} = \frac{g}{V}\frac{RT}{P} = d\frac{RT}{P}$$

Dalton's law of partial pressures (page 499)

$$P_{\text{total}} = P_A + P_B + P_C + \cdots$$

We use this law to calculate the partial pressure of one gas in a mixture of gases. This requires the total pressure and either the partial pressures of the other gases or their mole fractions. If the partial pressures are known, their sum is the total pressure. When a gas is collected over water, this law is used to obtain the partial pressure of the collected gas in the "wet" gas mixture. $P_{\text{total}} = P_{\text{water}} + P_{\text{gas}}$

Mole fractions (pages 502 and 503)

$$X_A = \frac{n_A}{n_{\text{total}}} = \frac{P_A}{P_{\text{total}}}$$

Given the composition of a gas mixture, we can calculate the mole fraction of a component. The mole fraction can then be used to find the partial pressure of the component given the total pressure. If the total pressure and partial pressure of a component are known, we can calculate the mole fraction of the component.

Graham's law of effusion (page 504)

$$\frac{\text{effusion rate }(A)}{\text{effusion rate }(B)} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}$$

This law allows us to calculate relative rates of effusion of gases. It also allows us to calculate molecular masses from relative rates of effusion.

van der Walls equation of state for real gases (page 514)

$$\left(P_{\text{meas}} + \frac{n^2 a}{V^2}\right)(V_{\text{meas}} - nb) = nRT$$

This law makes adjustments for the fact that gas molecules may have attractive forces and that gas molecules have a finite volume.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Concept of Pressure; Manometers and Barometers

11.1 If you get jabbed by a pencil, why does it hurt so much more if it's with the sharp point rather than the eraser? Explain in terms of the concepts of force and pressure.

11.2 Write expressions that could be used to form conversion factors to convert between:

(a) kilopascal and atm,

(b) torr and mm Hg,

(c) bar and pascal,

(d) torr and atm,

(e) torr and pascal,

(f) bar and atm

11.3 At 20 °C the density of mercury is 13.6 g mL^{-1} and that of water is 1.00 g mL^{-1}. At 20 °C, the vapor pressure of mercury is 0.0012 torr and that of water is 18 torr. Give and explain two reasons why water would be an inconvenient fluid to use in a Torricelli barometer.

11.4 What is the advantage of using a closed-end manometer, rather than an open-end one, when measuring the pressure of a trapped gas?

Gas Laws

11.5 Express the following gas laws in equation form: **(a)** temperature–volume law (Charles' law), **(b)** temperature–pressure law (Gay-Lussac's law), **(c)** pressure–volume law (Boyle's law), **(d)** combined gas law

11.6 Which of the four important variables in the study of the physical properties of gases are assumed to be held constant in each of the following laws? **(a)** Boyle's law, **(b)** Charles' law, **(c)** Gay-Lussac's law, **(d)** combined gas law

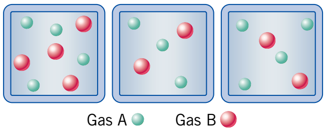
11.7 What is meant by an *ideal gas*? Under what conditions does a real gas behave most like an ideal gas? State the ideal gas law in the form of an equation. What is the value of the gas constant in units of L atm mol^{-1} K^{-1}?

11.8 Determine how to plot the two properties of gases listed with each of the following gas laws so that the graph will be a straight line. **(a)** temperature–volume law (Charles' law), **(b)** temperature–pressure law (Gay Lussac's law), **(c)** pressure–volume law (Boyle's law)

11.9 State Dalton's law of partial pressures in the form of an equation.

11.10 Define mole fraction. How is the partial pressure of a gas related to its mole fraction and the total pressure?

11.11 Consider the diagrams below that illustrate three mixtures of gases *A* and *B*. If the total pressure of the mixture is 1.00 atm, which of the drawings corresponds to a mixture in which the partial pressure of *A* equals 0.600 atm? What are the partial pressures of *A* in the other mixtures? What are the partial pressures of *B*?



11.12 What is the difference between *diffusion* and *effusion*? State Graham's law in the form of an equation.

Kinetic Theory of Gases

11.13 Describe the model of a gas proposed by the kinetic theory of gases?

11.14 If the molecules of a gas at constant volume are somehow given a lower average kinetic energy, what two measurable properties of the gas will change and in what direction?

11.15 Explain *how* raising the temperature of a gas causes it to expand at constant pressure. (*Hint:* Describe how the model of an ideal gas connects the increase in temperature to the gas expansion.)

11.16 Explain in terms of the kinetic theory how raising the temperature of a confined gas makes its pressure increase.

11.17 How does the kinetic theory explain the existence of an absolute zero, 0 K?

11.18 Which of the following gases has the largest value of $\overline{v_{\text{rms}}}$ at 25 °C: **(a)** N_2, **(b)** CO_2, **(c)** NH_3, or **(d)** HBr?

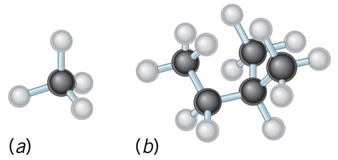
11.19 How would you expect the rate of effusion of a gas to depend on **(a)** the pressure of the gas, and **(b)** the temperature of the gas?

Real Gases

11.20 Which postulates of the kinetic theory are not strictly true, and why?

11.21 What does a small value for the van der Waals constant *a* suggest about the molecules of the gas?

11.22 Which of the molecules below has the larger value of the van der Waals constant *b*? Explain your choice.



11.23 Under the same conditions of *T* and *V*, why is the pressure of a real gas less than the pressure the gas would exert if it were ideal? At a given *T* and *P*, why is the volume of a real gas larger than it would be if the gas were ideal?

11.24 Suppose we have a mixture of helium and argon. On average, which atoms are moving faster at 25 °C, and why?

| Review Problems

Pressure Unit Conversions

OH **11.25** Carry out the following unit conversions: **(a)** 1.26 atm to torr, **(b)** 740 torr to atm, **(c)** 738 torr to mm Hg, **(d)** 1.45×10^3 Pa to torr.

11.26 Carry out the following unit conversions: **(a)** 0.625 atm to torr, **(b)** 825 torr to atm, **(c)** 62 mm Hg to torr, **(d)** 1.22 kPa to bar.

11.27 What is the pressure in torr of each of the following?

(a) 0.329 atm (summit of Mt. Everest, the world's highest mountain)

(b) 0.460 atm (summit of Mt. Denali, the highest mountain in the United States)

11.28 What is the pressure in atm of each of the following? (These are the values of the pressures exerted individually by N_2, O_2, and CO_2, respectively, in typical inhaled air.)

(a) 595 torr **(b)** 160 torr **(c)** 0.300 torr

Manometers and Barometers

11.29 An open-end manometer containing mercury was connected to a vessel holding a gas at a pressure of 720 torr. The atmospheric pressure was 765 torr. Sketch a diagram of the apparatus showing the relative heights of the mercury in the two arms of the manometer. What is the difference in the heights of the mercury expressed in centimeters?

11.30 An open-end manometer containing mercury was connected to a vessel holding a gas at a pressure of 820 torr. The atmospheric pressure was 750 torr. Sketch a diagram of the apparatus showing the relative heights of the mercury in the two arms of the manometer. What is the difference in the heights of the mercury expressed in centimeters?

11.31 An open-end mercury manometer was connected to a flask containing a gas at an unknown pressure. The mercury in the arm open to the atmosphere was 65 mm higher than the mercury in the arm connected to the flask. The atmospheric pressure was 748 torr. What was the pressure of the gas in the flask (in torr)?

11.32 An open-end mercury manometer was connected to a flask containing a gas at an unknown pressure. The mercury in the arm open to the atmosphere was 82 mm lower than the mercury in the arm connected to the flask. The atmospheric pressure was 752 torr. What was the pressure of the gas in the flask (in torr)?

11.33 Suppose that in a closed-end manometer the mercury in the closed arm was 12.5 cm higher than the mercury in the arm connected to a vessel containing a gas. What is the pressure of the gas expressed in torr?

11.34 Suppose a gas is in a vessel connected to both an open-end and a closed-end manometer. The difference in heights of the mercury in the closed-end manometer was 236 mm, while in the open-end manometer the mercury level in the arm open to the atmosphere was 512 mm below the level in the arm connected to the vessel. Calculate the atmospheric pressure. (It may help to sketch the apparatus.)

Gas Laws for a Fixed Amount of Gas

11.35 A gas has a volume of 255 mL at 725 torr. What volume will the gas occupy at 365 torr if the temperature of the gas doesn't change?

11.36 A bicycle pump has a barrel that is 75.0 cm long (about 30 in.). If air is drawn into the pump at a pressure of 1.00 atm during the upstroke, how long must the downstroke be, in centimeters, to raise the pressure of the air to 5.50 atm (approximately the pressure in the tire of a 10-speed bike)? Assume no change in the temperature of the air.

11.37 A gas has a volume of 3.86 L at 45 °C. What will the volume of the gas be if its temperature is raised to 87 °C while its pressure is kept constant?

OH **11.38** A balloon has a volume of 2.50 L indoors at 22 °C. If the balloon is taken outdoors on a cold day when the air temperature is −15 °C (5 °F), what will its volume be in liters? Assume constant air pressure within the balloon.

11.39 A sample of a gas has a pressure of 854 torr at 285 °C. To what Celsius temperature must the gas be heated to double its pressure if there is no change in the volume of the gas?

11.40 Before taking a trip, you check the air in a tire of your automobile and find it has a pressure of 45 lb in.$^{-2}$ on a day when the air temperature is 12 °C (54 °F). After traveling some distance, you find that the temperature of the air in the tire has risen to 43 °C (approximately 109 °F). What is the air pressure in the tire at this higher temperature, expressed in units of lb in.$^{-2}$?

ILW **11.41** A sample of helium at a pressure of 745 torr and in a volume of 2.58 L was heated from 24.0 to 75.0 °C. The volume of the container expanded to 2.81 L. What was the final pressure (in torr) of the helium?

11.42 When a sample of neon with a volume of 648 mL and a pressure of 0.985 atm was heated from 16.0 to 63.0 °C, its volume became 689 mL. What was its final pressure (in atm)?

11.43 What must be the new volume of a sample of nitrogen (in L) if 2.68 L at 745 torr and 24.0 °C is heated to 375.0 °C under conditions that let the pressure change to 765 torr?

11.44 When 286 mL of oxygen at 741 torr and 18.0 °C was warmed to 33.0 °C, the pressure became 765 torr. What was the final volume (in mL)?

11.45 A sample of argon with a volume of 6.18 L, a pressure of 761 torr, and a temperature of 20.0 °C expanded to a volume of 9.45 L and a pressure of 373 torr. What was its final temperature in °C?

11.46 A sample of a refrigeration gas in a volume of 455 mL, at a pressure of 1.51 atm and at a temperature of 25.0 °C, was compressed into a volume of 222 mL with a pressure of 2.00 atm. To what temperature (in °C) did it have to change?

Ideal Gas Law

11.47 What would be the value of the gas constant R in units of mL torr mol^{-1} K^{-1}?

11.48 The SI generally uses its base units to compute constants involving derived units. The SI unit for volume, for example, is the cubic meter, called the *stere*, because the meter is the base unit of length. We learned about the SI unit of pressure, the pascal, in this chapter. The temperature unit is the kelvin. Calculate the value of the gas constant in the SI units, m^3 Pa mol^{-1} K^{-1}.

11.49 What volume in liters does 0.136 g of O_2 occupy at 20.0 °C and 748 torr?

11.50 What volume in liters does 1.67 g of N_2 occupy at 22.0 °C and 756 torr?

11.51 What pressure (in torr) is exerted by 10.0 g of O_2 in a 2.50 L container at a temperature of 27 °C?

11.52 If 12.0 g of water is converted to steam in a 3.60 L pressure cooker held at a temperature of 108 °C, what pressure will be produced?

11.53 A sample of carbon dioxide has a volume of 26.5 mL at 20.0 °C and 624 torr. How many grams of CO_2 are in the sample?

11.54 Methane is formed in landfills by the action of certain bacteria on buried organic matter. If a sample of methane collected from a landfill has a volume of 255 mL at 758 torr and 27 °C, how many grams of methane are in the sample?

11.55 To three significant figures, calculate the density in g L^{-1} of the following gases at STP: **(a)** C_2H_6 (ethane), **(b)** N_2, **(c)** Cl_2, **(d)** Ar.

11.56 To three significant figures, calculate the density in g L^{-1} of the following gases at STP: **(a)** Ne, **(b)** O_2, **(c)** CH_4 (methane), **(d)** CF_4.

OH **11.57** What density (in g L^{-1}) does oxygen have at 24.0 °C and 742 torr?

11.58 At 748.0 torr and 20.65 °C, what is the density of argon (in g L^{-1})?

ILW **11.59** A chemist isolated a gas in a glass bulb with a volume of 255 mL at a temperature of 25.0 °C and a pressure (in the bulb) of 10.0 torr. The gas weighed 12.1 mg. What is the molar mass of this gas?

11.60 At 22.0 °C and a pressure of 755 torr, a gas was found to have a density of 1.13 g L^{-1}. Calculate its molar mass.

Stoichiometry of Reactions of Gases

11.61 How many milliliters of oxygen are required to react completely with 175 mL of C_4H_{10} if the volumes of both gases are measured at the same temperature and pressure? The reaction is

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

OH **11.62** How many milliliters of O_2 are consumed in the complete combustion of a sample of hexane, C_6H_{14}, if the reaction produces 855 mL of CO_2? Assume all gas volumes are measured at the same temperature and pressure. The reaction is

$$2C_6H_{14}(g) + 19O_2(g) \longrightarrow 12CO_2(g) + 14H_2O(g)$$

ILW **11.63** Propylene, C_3H_6, reacts with hydrogen under pressure to give propane, C_3H_8:

$$C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g)$$

How many liters of hydrogen (at 740 torr and 24 °C) react with 18.0 g of propylene?

11.64 Nitric acid is formed when NO_2 is dissolved in water.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

How many milliliters of NO_2 at 25 °C and 752 torr are needed to form 12.0 g of HNO_3?

11.65 How many milliliters of O_2 measured at 27 °C and 654 torr are needed to react completely with 16.8 mL of CH_4 measured at 35 °C and 725 torr?

11.66 How many milliliters of H_2O vapor, measured at 318 °C and 735 torr, are formed when 33.6 mL of NH_3 at 825 torr and 127 °C react with oxygen according to the following equation?

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$$

11.67 Calculate the maximum number of milliliters of CO_2, at 745 torr and 27 °C, that could be formed in the combustion of carbon monoxide if 0.300 L of CO at 683 torr and 25 °C is mixed with 155 mL of O_2 at 715 torr and 125 °C.

11.68 A mixture of ammonia and oxygen is prepared by combining 0.300 L of N_2 (measured at 0.750 atm and 28 °C) with 0.220 L of O_2 (measured at 0.780 atm and 50 °C). How many milliliters of N_2 (measured at 0.740 atm and 100.0 °C) could be formed if the following reaction occurs?

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$$

Dalton's Law of Partial Pressures

***11.69** OH A 1.00 L container was filled by pumping into it 1.00 L of N_2 at 20.0 cm Hg, 1.00 L of O_2 at 155 torr, and 1.00 L of He at 0.450 atm. All volumes and pressures were measured at the same temperature. What was the total pressure inside the container after the mixture was made?

11.70 A mixture of N_2, O_2, and CO_2 has a total pressure of 740 torr. In this mixture the partial pressure of N_2 is 12.0 cm Hg and the partial pressure of O_2 is 4.00 dm Hg. What is the partial pressure of the CO_2?

ILW **11.71** A 22.4 L container at 0 °C contains 0.30 mol N_2, 0.20 mol O_2, 0.40 mol He, and 0.10 mol CO_2. What are the partial pressures of each of the gases in torr, atm, and bar?

11.72 A 0.200 mol sample of a mixture of N_2 and CO_2 with a total pressure of 845 torr was exposed to an excess of solid CaO, which reacts with CO_2 according to the equation

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$

After the reaction was complete, the pressure of the gas had dropped to 322 torr. How many moles of CO_2 were in the original mixture? (Assume no change in volume or temperature.)

11.73 A sample of carbon monoxide was prepared and collected over water at a temperature of 22 °C and a total pressure of 754 torr. It occupied a volume of 268 mL. Calculate the partial pressure of the CO in torr as well as its dry volume (in mL) under a pressure of 1.00 atm and 25 °C.

11.74 A sample of hydrogen was prepared and collected over water at 25 °C and a total pressure of 742 torr. It occupied a volume of 288 mL. Calculate its partial pressure (in torr) and what its dry volume would be (in mL) under a pressure of 1.00 atm at 25 °C.

11.75 What volume of "wet" methane would you have to collect at 20.0 °C and 742 torr to be sure that the sample contains 244 mL of dry methane (also at 742 torr)?

11.76 What volume of "wet" oxygen would you have to collect if you need the equivalent of 275 mL of dry oxygen at 1.00 atm? (The atmospheric pressure in the lab is 746 torr.) The oxygen is to be collected over water at 15.0 °C.

Graham's Law

11.77 Under conditions in which the density of CO_2 is 1.96 g L^{-1} and that of N_2 is 1.25 g L^{-1}, which gas will effuse more rapidly? What will be the ratio of the rates of effusion of N_2 to CO_2?

11.78 Arrange the following gases in order of increasing rate of diffusion at 25 °C: Cl_2, C_2H_4, SO_2.

11.79 Uranium hexafluoride is a white solid that readily passes directly into the vapor state. (Its vapor pressure at 20.0 °C is 120 torr.) A trace of the uranium in this compound—about 0.7%—is uranium-235, which can be used in a nuclear power plant. The rest of the uranium is essentially uranium-238, and its presence interferes with these applications for uranium-235. Gas effusion of UF_6 can be used to separate the fluoride made from uranium-235 and the fluoride made from uranium-238. Which hexafluoride effuses more rapidly? By how much? (You can check your answer by reading Chemistry and Current Affairs 11.1 on page 505.)

OH **11.80** An unknown gas *X* effuses 1.65 times faster than C_3H_8. What is the molecular mass of gas *X*?

Additional Problems

11.81 One of the oldest units for atmospheric pressure is lb in.$^{-2}$ (pounds per square inch, or psi). Calculate the numerical value of the standard atmosphere in these units to three significant figures. Calculate the mass in pounds of a uniform column of water 33.9 ft high having an area of 1.00 in.^{2} at its base. (Use the following data: density of mercury = 13.6 g mL^{-1}; density of water = 1.00 g mL^{-1}; 1 mL = 1 cm^3; l lb = 454 g; 1 in. = 2.54 cm.)

***11.82** A typical automobile has a weight of approximately 3500 lb. If the vehicle is to be equipped with tires, each of which will contact the pavement with a "footprint" that is 6.0 in. wide by 3.2 in. long, what must the gauge pressure of the air be in each tire? (Gauge pressure is the amount that the gas pressure exceeds atmospheric pressure. Assume that atmospheric pressure is 14.7 lb in.$^{-2}$.)

***11.83** Suppose you were planning to move a house by transporting it on a large trailer. The house has an estimated weight of 45.6 tons (1 ton = 2000 lb). The trailer is expected to weigh 8.3 tons. Each wheel of the trailer will have tires inflated to a gauge pressure of 85 psi (which is actually 85 psi above atmospheric pressure). If the area of contact between a tire and the pavement can be no larger than 100.0 in.^{2} (10.0 in. × 10.0 in.), what is the minimum number of wheels the trailer must have? (Remember, tires are mounted in multiples of two on a trailer. Assume that atmospheric pressure is 14.7 psi.)

***11.84** The motion picture *Titanic* described the tragedy of the collision of the ocean liner of the same name with an iceberg in the North Atlantic. The ship sank soon after the collision on April 14, 1912, and now rests on the sea floor at a depth of 12,468 ft. Recently, the wreck was explored by the research vessel *Nautile*, which has successfully recovered a variety of items from the debris field surrounding the sunken ship. Calculate the pressure in atmospheres and pounds per square inch exerted on the hull of the *Nautile* as it explores the sea bed surrounding the *Titanic*. (*Hint:* The height of a column of liquid required to exert a given pressure is inversely proportional to the liquid's density. Seawater has a density of approximately 1.025 g mL^{-1}; mercury has a density of 13.6 g mL^{-1}; 1 atm = 14.7 lb $in.^{-2}$.)

***11.85** Two flasks (which we will refer to as flask 1 and flask 2) are connected to each other by a U-shaped tube filled with an oil having a density of 0.826 g mL^{-1}. The oil level in the arm connected to flask 2 is 16.24 cm higher than in the arm connected to flask 1. Flask 1 is also connected to an open-end mercury manometer. The mercury level in the arm open to the atmosphere is 12.26 cm higher than the level in the arm connected to flask 1. The atmospheric pressure is 0.827 atm. What is the pressure of the gas in flask 2 expressed in torr? (See the hint given in Problem 11.84.)

***11.86** OH A bubble of air escaping from a diver's mask rises from a depth of 100 ft to the surface where the pressure is 1.00 atm. Initially, the bubble has a volume of 10.0 mL. Assuming none of the air dissolves in the water, how many times larger is the bubble just as it reaches the surface? Use your answer to explain why scuba divers constantly exhale as they slowly rise from a deep dive. (The density of seawater is approximately 1.025 g mL^{-1}; the density of mercury is 13.6 g mL^{-1}.)

***11.87** In a diesel engine, the fuel is ignited when it is injected into hot compressed air, heated by the compression itself. In a typical high-speed diesel engine, the chamber in the cylinder has a diameter of 10.7 cm and a length of 13.4 cm. On compression, the length of the chamber is shortened by 12.7 cm (a "5-inch stroke"). The compression of the air changes its pressure from 1.00 to 34.0 atm. The temperature of the air before compression is 364 K. As a result of the compression, what will be the final air temperature (in K and °C) just before the fuel injection?

***11.88** Early one cool (60.0 °F) morning you start on a bike ride with the atmospheric pressure at 14.7 lb $in.^{-2}$ and the tire gauge pressure at 50.0 lb $in.^{-2}$. (Gauge pressure is the amount that the pressure exceeds atmospheric pressure.) By late afternoon, the air had warmed up considerably, and this plus the heat generated by tire friction sent the temperature inside the tire to 104 °F. What will the tire gauge now read, assuming that the volume of the air in the tire and the atmospheric pressure have not changed?

OH **11.89** The range of temperatures over which an automobile tire must be able to withstand pressure changes is roughly −50 to 120 °F. If a tire is filled to 35 lb $in.^{-2}$ at −35 °F (on a cold day in Alaska, for example), what will be the pressure in the tire (in the same pressure units) on a hot day in Death Valley when the temperature is 115 °F? (Assume that the volume of the tire does not change.)

OH **11.90** A mixture was prepared in a 0.500 L reaction vessel from 0.300 L of O_2 (measured at 25 °C and 74.0 cm Hg) and 0.400 L of H_2 (measured at 45 °C and 1250 torr). The mixture was ignited and the H_2 and O_2 reacted to form water. What was the final pressure inside the reaction vessel after the reaction was over if the temperature was held at 122 °C?

11.91 A student collected 18.45 mL of H_2 over water at 24 °C. The water level inside the collection apparatus was 8.5 cm higher than the water level outside. The barometric pressure was 746 torr. How many grams of zinc had to react with HCl(*aq*) to produce the H_2 that was collected?

11.92 A mixture of gases is prepared from 87.5 g of O_2 and 12.7 g of H_2. After the reaction of O_2 and H_2 is complete, what is the total pressure of the mixture if its temperature is 162 °C and its volume is 12.0 L? What are the partial pressures of the gases remaining in the mixture?

11.93 A gas was found to have a density of 0.08747 mg mL^{-1} at 17.0 °C and a pressure of 1.00 atm. What is its molecular mass? Can you tell what the gas most likely is?

***11.94** In one analytical procedure for determining the percentage of nitrogen in unknown compounds, weighed samples are made to decompose to N_2, which is collected over water at known temperatures and pressures. The volumes of N_2 are then translated into grams and then into percentages.

(a) Show that the following equation can be used to calculate the percentage of nitrogen in a sample having a mass of W grams when the N_2 has a volume of V mL and is collected over water at t_c °C at a total pressure of P torr. The vapor pressure of water occurs in the equation as $P^{\circ}_{H_2O}$.

$$\text{Percentage N} = 0.04489 \times \frac{V(P - P^{\circ}_{H_2O})}{W(273 + t_c)}$$

(b) Use this equation to calculate the percentage of nitrogen in the sample described in Problem 11.97.

Multi-Concept Problems

***11.95** A common laboratory preparation of hydrogen on a small scale uses the reaction of zinc with hydrochloric acid. Zinc chloride is the other product.

(a) If 12.0 L of H_2 at 765 torr and 20.0 °C is wanted, how many grams of zinc are needed, in theory?

(b) If the acid is available as 8.00 M HCl, what is the minimum volume of this solution (in milliliters) required to produce the amount of H_2 described in part (a)?

***11.96** A sample of an unknown gas with a mass of 3.620 g was made to decompose into 2.172 g of O_2 and 1.448 g of S. Before the decomposition, this sample occupied a volume of 1120 mL at 75.0 cm Hg and 25.0 °C. What is the molecular formula of this gas?

***11.97** A sample of a new anti-malarial drug with a mass of 0.2394 g was made to undergo a series of reactions that changed all of the nitrogen in the compound into N_2. This gas had a volume of 18.90 mL when collected over water at 23.80 °C and a pressure of 746.0 torr. At 23.80 °C, the vapor pressure of water is 22.110 torr. When 6.478 mg of the compound was burned in pure oxygen, 17.57 mg of CO_2 and 4.319 mg of H_2O were obtained. What are the percentages of C and H in this compound?

(a) Assuming that any undetermined element is oxygen, write an empirical formula for the compound.

(b) The molecular mass of the compound was found to be 324. What is its molecular formula?

11.98 The odor of a rotten egg is caused by hydrogen sulfide, H_2S. Most people can detect it at a concentration of 0.15 ppb (parts per billion), meaning 0.15 L of H_2S in 10^9 L of space. A typical student lab is 42 × 24 × 8.6 ft.

(a) At STP, how many liters of H_2S could be present in a typical lab to have a concentration of 0.15 ppb?

(b) How many milliliters of 0.100 M Na_2S would be needed to generate the amount of H_2S in part (a) by the reaction of hydrochloric acid with sodium sulfide? (Assume that all of the H_2S generated enters the atmosphere.)

11.99 Chlorine reacts with sulfite ion to give sulfate ion and chloride ion. How many milliliters of Cl_2 gas measured at 25 °C and 734 torr are required to react with all the SO_3^{2-} in 50.0 mL of 0.200 M Na_2SO_3 solution?

***11.100** In an experiment designed to prepare a small amount of hydrogen by the method described in Problem 11.95, a student was limited to using a gas-collecting bottle with a maximum capacity of 335 mL. The method involved collecting the hydrogen over water. What are the minimum number of grams of Zn and the minimum number of milliliters of 6.00 M HCl needed to produce the *wet* hydrogen that can exactly fit this collecting bottle at 0.932 atm and 25.0 °C?

***11.101** Carbon dioxide can be made in the lab by the reaction of hydrochloric acid with calcium carbonate. How many milliliters of dry CO_2 at 20.0 °C and 745 torr can be prepared from a mixture of 12.3 g of $CaCO_3$ and 185 mL of 0.250 M HCl?

11.102 Boron forms a variety of unusual compounds with hydrogen. A chemist isolated 6.3 mg of one of the boron hydrides in a glass bulb with a volume of 385 mL at 25.0 °C and a bulb pressure of 11 torr. Which of the following is likely to be its molecular formula: BH_3, B_2H_6, or B_4H_{10}?

Exercises in Critical Thinking

11.103 Firefighters advise that you get out of a burning building by keeping close to the floor. We learned that carbon dioxide and most other hazardous compounds are more dense than air and they should settle to the floor. What other facts do we know that make the firefighter's advice correct?

11.104 Carbon dioxide is implicated in global warming. Propose ways to control or perhaps decrease the carbon dioxide content in our air. Rank each proposal based on its feasibility.

11.105 Methane is another gas implicated in the global warming problem. It has been proposed that much of the methane in the atmosphere is from ruminating cows. Evaluate that suggestion and come up with other possible sources of methane.

***11.106** One of the CFCs that is implicated in decreasing the ozone layer and formation of the ozone hole over Antarctica is Freon-12 or CCl_2F_2. Calculate the density of Freon-12 at STP and compare it to the average density of air. Suggest how Freon-12 can get into the stratosphere to threaten the ozone layer.

12 Intermolecular Attractions and the Properties of Liquids and Solids

Chapter Outline

12.1 | Gases, Liquids, and Solids and Intermolecular Distances

12.2 | Types of Intermolecular Forces

12.3 | Intermolecular Forces and Properties of Liquids and Solids

12.4 | Changes of State and Dynamic Equilibria

12.5 | Vapor Pressures of Liquids and Solids

12.6 | Boiling Points of Liquids

12.7 | Energy and Changes of State

12.8 | Determining Heats of Vaporization

12.9 | Le Châtelier's Principle and State Changes

12.10 | Phase Diagrams

12.11 | Structures of Crystalline Solids

12.12 | X-Ray Diffraction of Solids

12.13 | Crystal Types and Physical Properties

On January 15, 2009, the US Airways flight 1549 left New York's LaGuardia Airport bound for Charlotte, NC, and after hitting a flock of geese and losing power in both engines, the pilot ditched the plane into the Hudson River. All of the passengers and crew survived. One question that arises from the plane floating on the water is what kept the plane afloat? In this chapter, we will look at how the molecules in a substance, such as water, interact with each other and affect the physical properties of the substance. Brendan McDermind/Reuters/© Corbis

This Chapter in Context

In Chapter 11 we studied the physical properties of gases, and we learned that all gases behave pretty much alike, regardless of their chemical composition. However, when we compare substances in their liquid or solid states (their *condensed states*), the situation is quite different. When a substance is a liquid or a solid, its particles are packed closely together and the forces between them, which we call *intermolecular forces*, are quite strong. Chemical composition and molecular structure play an important role in determining the strengths of such forces, and this causes substances to behave quite differently from each other when they are liquids or solids.

In this chapter, we focus our attention on the properties of liquids and solids. We begin our study by looking at the basic differences among the states of matter in terms of both common observable properties and the way the states of matter differ at the molecular level. We will also examine the different kinds and relative strengths of intermolecular forces. You will learn how they are related to molecular composition and structure, and how intermolecular forces influence a variety of familiar physical properties of liquids, such as boiling points and the ease of evaporation. And, by studying the energy changes associated with changes of states (for example, evaporation or condensation), you will become familiar with the forces that affect practical applications ranging from evaporative air-conditioning to weather prediction. Finally, we will discuss the structure and properties of crystalline solids such as the gold pictured on the front cover of the book and common table salt.

12.1 | Gases, Liquids, and Solids and Intermolecular Distances

There are differences among gases, liquids, and solids that are immediately obvious and familiar to everyone. For example, any gas will expand to fill whatever volume is available, even if it has to mix with other gases to do so. Liquids and solids, however, retain a constant volume when transferred from one container to another. A solid, such as an ice cube, also keeps its shape, but a liquid such as soda conforms to the shape of whatever bottle or glass we put it in.

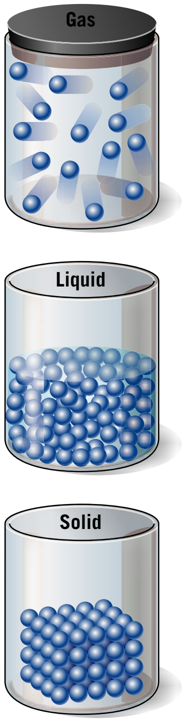
In Chapter 11 you learned that gases are easily compressed. Liquids and solids, on the other hand, are nearly *incompressible*, which means their volumes change very little when they are subjected to high pressures. Properties such as the ones we've described can be understood in terms of the way the particles are distributed in the three states of matter, which is summarized in Figure 12.1.

Distance and Intermolecular Forces

If you've ever played with magnets, you know that their mutual attraction weakens rapidly as the distance between them increases. Intermolecular attractions are similarly affected by the distance between molecules, rapidly becoming weaker as the distance between the molecules increases.

■ The closer two molecules are, the more strongly they attract each other.

In gases, the molecules are so far apart that intermolecular attractions are almost negligible, so differences between the attractive forces hardly matter. As a result, chemical composition has little effect on the properties of a gas. However, in a liquid or a solid, the molecules are close together and the attractions are strong. Differences among these attractions caused by differences in chemical makeup are greatly amplified, so the properties of liquids and solids depend quite heavily on chemical composition.



	Observable Properties	Molecular Properties
Gas	Easily compressed Expand spontaneously to fill container	Widely spaced molecules with much empty space between them Random motion Very weak attractions between the molecules
Liquid	Retain volume Conform to shape of the container Able to flow Nearly incompressible	Molecules tightly packed but little order Able to move past each other with little difficulty Intermolecular attractive forces relatively strong
Solid	Retain volume Retain shape Virtually incompressible Often have crystalline shape	Molecules tightly packed and highly ordered Molecules locked in place Very strong molecular forces

Figure 12.1 | **General properties of gases, liquids, and solids.** Properties can be understood in terms of the tightness of molecular packing and the strengths of the intermolecular attractions.

12.2 | Types of Intermolecular Forces

_Inter_molecular forces (the attractions *between* molecules) are always much weaker than the attractions between atoms *within* molecules (**_intra_molecular** forces, which are the *chemical bonds* that hold molecules together). In a molecule of NO, for example, the N and O atoms are held very tightly to each other by a covalent bond, and it is the strength of this bond that affects the *chemical properties* of NO. The strength of the chemical bond also keeps the molecule intact as it moves about. When a particular nitrogen atom moves, the oxygen atom bonded to it is forced to follow along (see Figure 12.2). Attractions between neighboring NO molecules, in contrast, are much weaker. In fact, they are only about 4% as strong as the covalent bond in NO. These weaker attractions are what determine the *physical properties* of liquid and solid NO.

There are several kinds of intermolecular attractions, which are discussed in this section. They all have something in common—namely, *they arise from attractions between opposite electrical charges*. Collectively, they are called **van der Waals forces**, after J. D. van der Waals, who studied the nonideal behavior of real gases.

TOOLS

Intermolecular attractions

London Forces

Nonpolar substances experience intermolecular attractions, as evidenced by the ability of the noble gases and nonpolar molecules such as Cl_2 and CH_4 to condense to liquids, and even to solids, when cooled to very low temperatures. In such liquids or solids, attractions between their particles must exist to cause them to cling together.

In 1930, Fritz London, a German physicist, explained how the particles in even nonpolar substances can experience intermolecular attractions. He noted that in any atom or molecule the electrons are constantly moving. If we could examine such motions in two neighboring particles, we would find that the

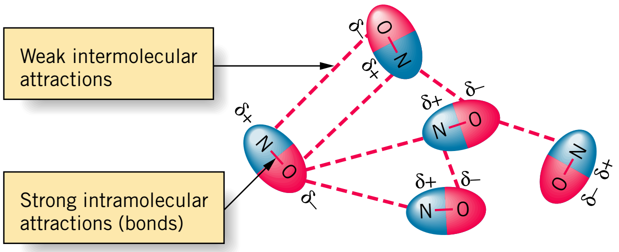
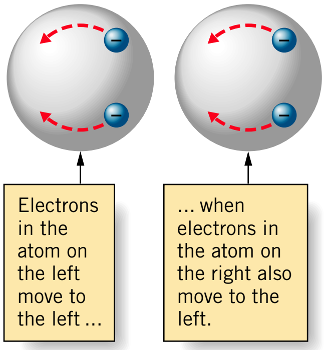

Weak intermolecular attractions
Strong intramolecular attractions (bonds)
δ–
O–N
δ+
δ+
δ–
N–O
δ+
N–O
δ–
δ+
δ–
N–O
O–N
δ+
δ–

Figure 12.2 | **Attractions within and between nitrogen monoxide molecules.** Strong *intramolecular* attractions (chemical bonds) exist between N and O atoms within NO molecules. These attractions control the chemical properties of NO. Weaker *intermolecular* attractions exist between neighboring NO molecules. The intermolecular attractions control the physical properties of this substance.


Electrons in the atom on the left move to the left ...
... when electrons in the atom on the right also move to the left.

movement of electrons in one influences the movement of electrons in the other. Because electrons repel each other, as an electron of one particle gets near the other particle, electrons on the second particle are pushed away. This happens continually as the electrons move around, so to some extent, the electron density in both particles flickers back and forth in a synchronous fashion. This is illustrated in Figure 12.3, which depicts a series of instantaneous "frozen" views of the electron density. Notice that *at any given moment the electron density of a particle can be unsymmetrical,* with more negative charge on one side than on the other. For that particular instant, the particle is a **dipole**, and we call it a momentary dipole or **instantaneous dipole**.

As an instantaneous dipole forms in one particle, it causes the electron density in its neighbor to become unsymmetrical, too. As a result, this second particle also becomes a dipole. We call it an **induced dipole** because it is caused by, or *induced* by, the formation of the first dipole. Because of the way the dipoles are formed, they always have the positive end of one near the negative end of the other, so there is an intermolecular attraction between the molecules. It is a very short-lived attraction, however, because the electrons keep moving; the dipoles vanish as quickly as they form. In another moment, however, the dipoles will reappear in a different orientation and there will be another brief *dipole–dipole attraction*. In this way the short-lived dipoles cause momentary tugs between the particles. When averaged over a period of time, there is a net overall attraction. It tends to be relatively weak, however, because the attractive forces are only "turned on" part of the time.

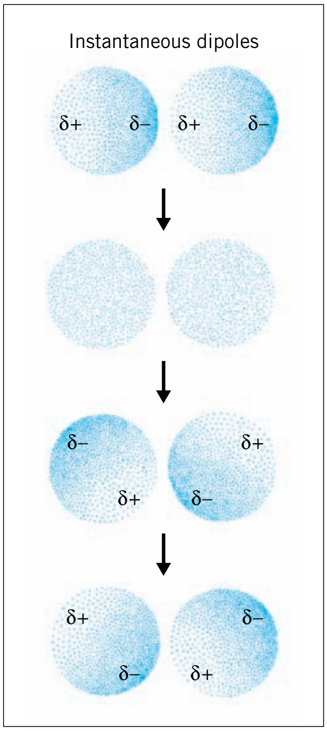


Figure 12.3 | **Instantaneous "frozen" views of the electron density in two neighboring particles.** Attractions exist between the instantaneous dipoles while they exist.

The momentary dipole–dipole attractions that we've just discussed are called *instantaneous dipole–induced dipole attractions*. They are also called **London dispersion forces** (or simply **London forces** or **dispersion forces**).

London forces exist between all molecules and ions. Although they are the only kind of attraction possible between nonpolar molecules, London forces even occur between oppositely charged ions, but their effects are relatively weak compared to ionic attractions.

■ London forces decrease very rapidly as the distance between particles increases. The energy required to separate particles held by London forces varies as $1/d^6$, where d is the distance between the particles.

The Strengths of London Forces

We can use boiling points to compare the strengths of intermolecular attractions. As we will explain in more detail later in this chapter, the higher the boiling point, the stronger are the attractions between molecules in the liquid.

The strengths of London forces depend chiefly on three factors. One is the **polarizability** of the electron cloud of a particle, which is a measure of the ease with which the electron cloud is distorted, and thus is a measure of the ease with which the instantaneous and induced dipoles can form. In general, *as the volume of the electron cloud increases, its polarizability also increases.* When an electron cloud is large, the outer electrons are generally not held very tightly by the nucleus (or nuclei, if the particle is a molecule). This causes the electron cloud to be "mushy" and rather easily deformed, so instantaneous dipoles and induced dipoles form without much difficulty (see Figure 12.4). As a result, particles with large electron clouds experience stronger London forces than do similar particles with small electron clouds.

The effects of size can be seen if we compare the boiling points of the halogens or the noble gases (see Table 12.1). As the atoms become larger, the boiling points increase, reflecting increasingly stronger intermolecular attractions (stronger London forces).

Table 12.1 Boiling Points of the Halogens and Noble Gases

Group 7A	Boiling Point (°C)	Group 8A	Boiling Point (°C)
F_2	−188.1	He	−268.6
Cl_2	−34.6	Ne	−245.9
Br_2	58.8	Ar	−185.7
I_2	184.4	Kr	−152.3
		Xe	−107.1
		Rn	−61.8

Table 12.2 Boiling Points of Some Hydrocarbons[a]

Molecular Formula	Boiling Point at 1 atm (°C)
CH_4	−161.5
C_2H_6	−88.6
C_3H_8	−42.1
C_4H_{10}	−0.5
C_5H_{12}	36.1
C_6H_{14}	68.7
⋮	⋮
$C_{10}H_{22}$	174.1
⋮	⋮
$C_{22}H_{46}$	327

[a] The molecules of each hydrocarbon in this table have carbon chains of the type C—C—C—C— etc.; that is, one carbon follows another and there are no branches in the carbon–carbon chain.

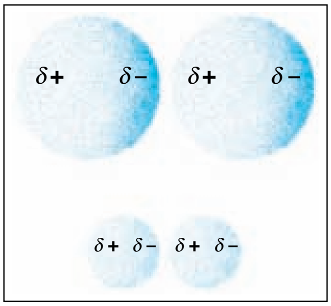


Figure 12.4 | **Effect of molecular size on the strengths of London dispersion forces.** A large electron cloud is more easily deformed than a small one, so in a large molecule the charges on opposite ends of an instantaneous dipole are larger than in a small molecule. Large molecules, therefore, experience stronger London forces than small molecules.

A second factor that affects the strengths of London forces is the number of atoms in a molecule. For molecules containing the same elements, London forces increase with the number of atoms, as illustrated by the hydrocarbons listed in Table 12.2. As the number of atoms increases, there are more places along their lengths where instantaneous dipoles can develop and lead to London attractions (Figure 12.5). Even if the strength of attraction at each location is about the same, the *total* attraction experienced between the longer molecules is greater.[1]

The third factor that affects the strengths of London forces is molecular shape. Even with molecules that have the same number of the same kinds of atoms, those that have compact shapes experience weaker London forces than long chain-like molecules (Figure 12.6). Presumably, because of the compact shape of the $(CH_3)_4C$ molecule, the area that can interact with a neighboring molecule is smaller than that of the chain-like $CH_3(CH_2)_3CH_3$ molecule.

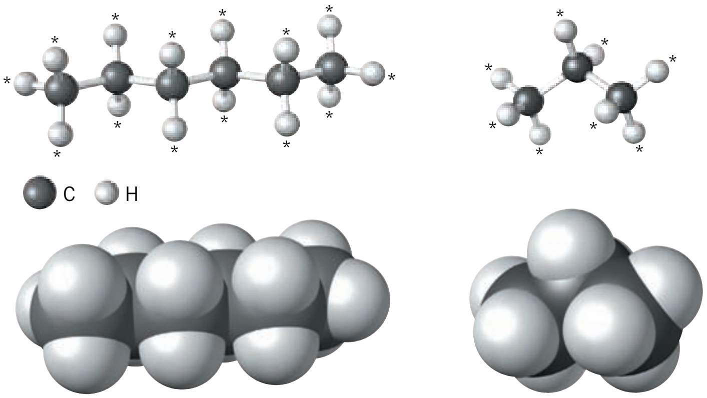


Figure 12.5 | **The number of atoms in a molecule affects London forces.** The C_6H_{14} molecule, *left*, shown as both a ball-and-stick model and a space-filling model, has more sites (indicated by asterisks, *) along its chain where it can be attracted to other molecules nearby than does the shorter C_3H_8 molecule, *right*. As a result, the boiling point of C_6H_{14} (hexane, 68.7 °C) is higher than that of C_3H_8 (propane, −42.1 °C).

---

[1] The effect of large numbers of atoms on the total strengths of London forces can be compared to the bond between loop and hook layers of Velcro. Each loop-to-hook attachment is not very strong, but when large numbers of them are involved, the overall bond between Velcro layers is quite strong.

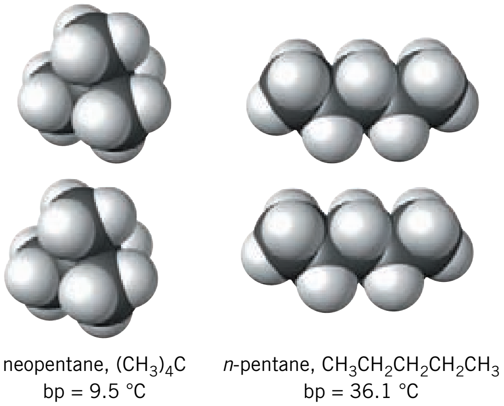
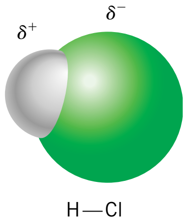


Figure 12.6 | **Molecular shape affects the strengths of London forces.** Shown at right are two compounds with the formula C_5H_{12}. Not all hydrogen atoms can be seen in these space-filling models. The compact neopentane molecule, $(CH_3)_4C$, has less area to interact with a neighboring molecule than the linear *n*-pentane molecule, $CH_3CH_2CH_2CH_2CH_3$, so overall the intermolecular attractions are weaker between the more compact molecules.

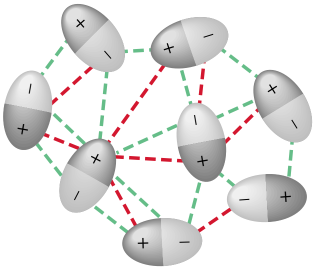
Dipole–Dipole Attractions



Polar molecules, such as HCl, have a partial positive charge at one end and a partial negative charge at the other, which is a permanent dipole. Because unlike charges attract, polar molecules tend to line up so the positive end of one dipole is near the negative end of another. However, molecules are in constant motion due to their thermal energy—that is, molecular kinetic energy—so they collide and become disoriented, and the alignment isn't perfect. Nevertheless, there is still a net attraction between them (Figure 12.7). We call this kind of intermolecular force a **dipole–dipole attraction** since the dipoles we're discussing here are full time, as opposed to the momentary dipoles responsible for London forces. Because collisions lead to substantial misalignment of the dipoles and because the attractions are only between partial charges, dipole–dipole forces are much weaker than covalent bonds, being only about 1–4 % as strong. Dipole–dipole attractions fall off rapidly with distance, with the energy required to separate a pair of dipoles being proportional to $1/d^3$, where d is the distance between the dipoles. In addition to the dipole–dipole interactions, the electrons in polar molecules can form instantaneous dipoles, so all polar molecules also experience London forces.

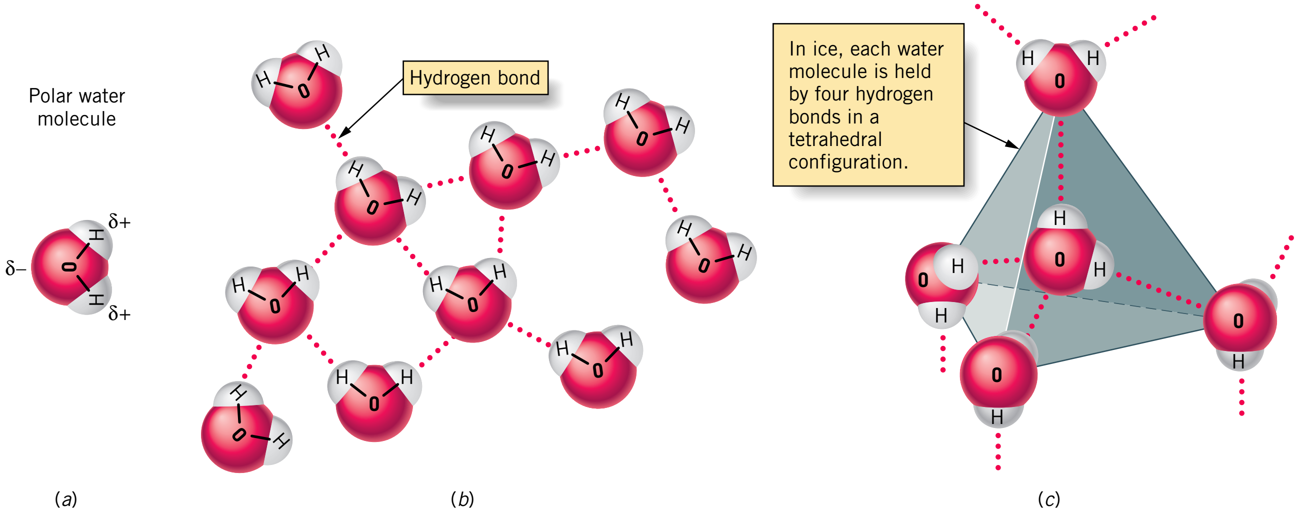
Hydrogen Bonds

When hydrogen is covalently bonded to a very small, highly electronegative atom (usually fluorine, oxygen, or nitrogen), a particularly strong type of dipole–dipole attraction occurs that's called **hydrogen bonding**. The electronegative atom pulls the electron density toward itself and gains a partial negative charge. In turn, the hydrogen carries a positive charge that attracts the partial negative charge of the next atom. Hydrogen bonds are exceptionally strong because F—H, O—H, and N—H bonds are very polar, and because the partial charges can get quite close since they are concentrated on very small atoms. Typically, a hydrogen bond is about five to ten times stronger than other dipole–dipole attractions.



Attractions (🟩) are greater than repulsions (🟥), so the molecules feel a net attraction to each other.

Figure 12.7 | **Dipole–dipole attractions.** Attractions between polar molecules occur because the molecules tend to align themselves so that opposite charges are near each other and like charges are as far apart as possible. The alignment is imperfect because the molecules are constantly moving and colliding.



In ice, each water molecule is held by four hydrogen bonds in a tetrahedral configuration.

Figure 12.8 | **Hydrogen bonding in water.** (*a*) The polar water molecule. (*b*) Hydrogen bonding produces strong attractions between water molecules in the liquid. (*c*) Hydrogen bonding (dotted lines) between water molecules in ice, where each water molecule is held by four hydrogen bonds in a tetrahedral configuration.

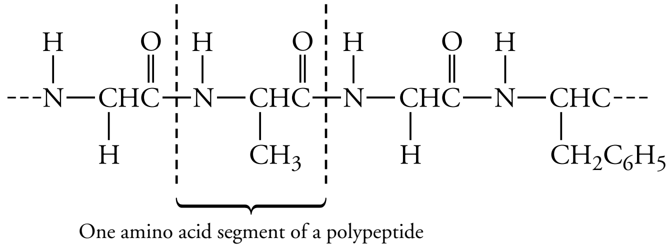
Hydrogen Bonds in Water and Biological Systems

Most substances become more dense when they change from a liquid to a solid. Water, however, is different (Figure 12.8). In liquid water, the molecules experience hydrogen bonds that continually break and re-form as the molecules move around (Figure 12.8*b*). As water begins to freeze, however, the molecules become locked in place, and each water molecule participates in four hydrogen bonds (Figure 12.8*c*). The resulting structure occupies a larger volume than the same amount of liquid water, so ice is less dense than the liquid. Because of this, ice cubes and icebergs float in the more dense liquid. The expansion of freezing water is capable of cracking a car's engine block, which is one reason we add antifreeze to a car's cooling system. Ice formation is also responsible for erosion, causing rocks to split where water has seeped into cracks. In northern cities, freezing water breaks up pavement, creating potholes in the streets.

■ A hydrogen bond is not a covalent bond. In water there are oxygen–hydrogen covalent bonds within H_2O molecules and hydrogen bonds between H_2O molecules.

Hydrogen bonding is especially important in biological systems because many molecules in our bodies contain N—H and O—H bonds. Examples are proteins and DNA. Proteins are made up mostly (in some cases, entirely) of long chains of amino acids, linked head to tail to form polypeptides. Shown below is part of a polypeptide chain:

■ Amino acids are discussed briefly in Chapter 23 on page 1083. Polypeptides are examples of *polymers*, which are large molecules made by linking together many smaller units called *monomers* (in this case, amino acids).



$$\text{---}\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{C}H\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{C}H\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle CH_2C_6H_5}{|}}{C}HC\text{---}$$

One amino acid segment of a polypeptide

Hydrogen bonding between N—H units in one part of the chain and the C═O groups in another part help determine the shape of the protein, which greatly influences its biological function. Hydrogen bonding is also responsible for the double helix structure of DNA, which carries our genetic information. This structure is illustrated in Figure 12.9.

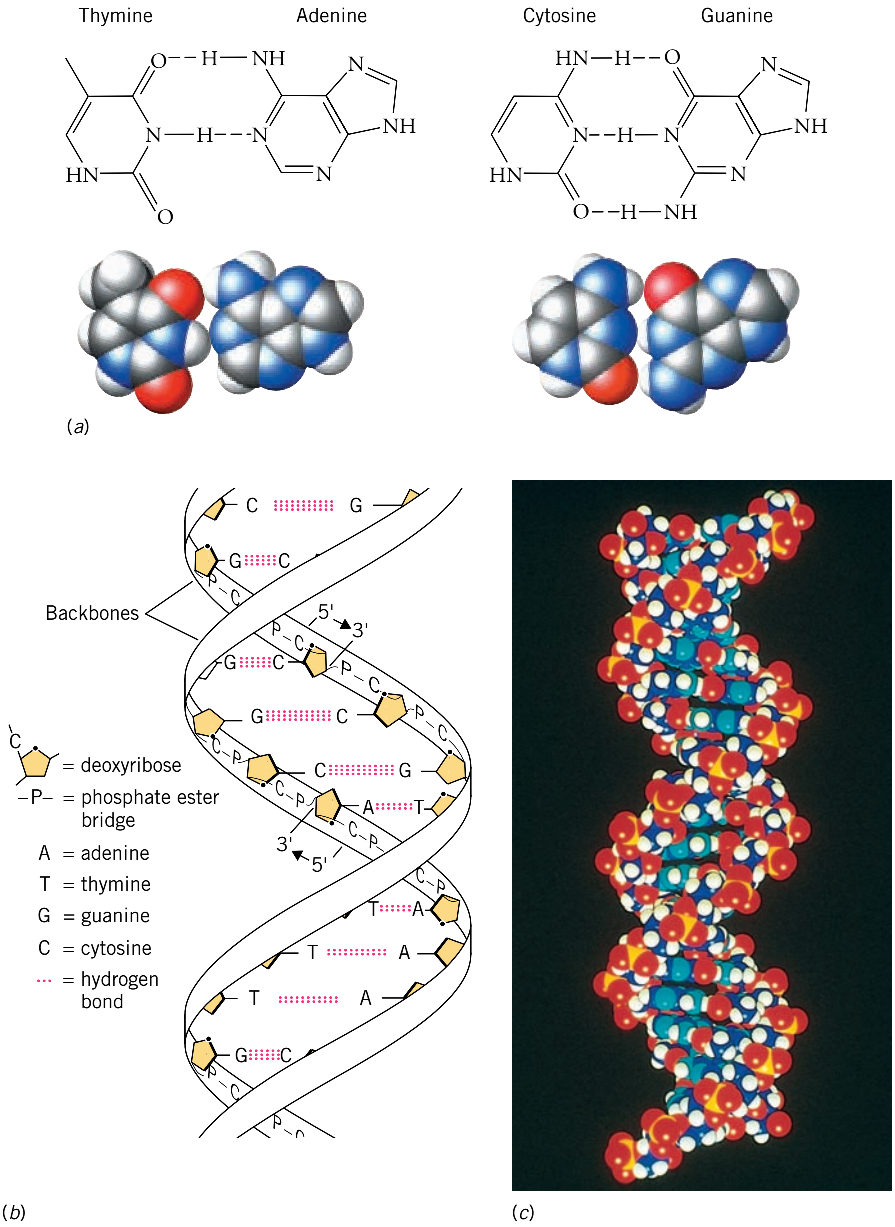

Thymine
Adenine
Cytosine
Guanine
O
H
NH
N
NH
HN
O
(a)
Backbones
5'
3'
C
G
A
T
P
= deoxyribose
–P– = phosphate ester bridge
A = adenine
T = thymine
G = guanine
C = cytosine
··· = hydrogen bond
(b)
(c)

Figure 12.9 | **Hydrogen bonding holds the DNA double helix together.** (*a*) The hydrogen bonding between the adenine and thymine, and guanine and cytosine of DNA. (*b*) A schematic drawing in which the hydrogen bonds between the two strands are indicated by dashed lines. The legend to the left of the structure describes the various components of the DNA molecule. (*c*) A model of a short section of a DNA double helix. The carbon atoms are shown in blue to distinguish them from the black background.

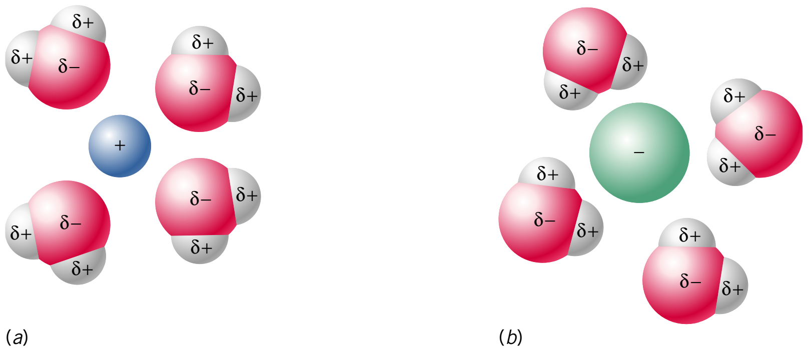


Figure 12.10 | **Ion–dipole attractions between water molecules and ions.** (*a*) The negative ends of water dipoles surround a cation and are attracted to the ion. (*b*) The positive ends of water molecules surround an anion, which gives a net attraction.

Ion–Dipole and Ion–Induced Dipole Forces of Attraction

In addition to the attractions that exist between neutral molecules, which we discussed above, there are also forces that arise when ions interact with molecules. For example, ions are able to attract the charged ends of polar molecules to give **ion–dipole attractions**. This occurs in water, for example, when ionic compounds dissolve to give hydrated ions. Cations become surrounded by water molecules that are oriented with the negative ends of their dipoles pointing toward the cation. Similarly, anions attract the positive ends of water dipoles. This is illustrated in Figure 12.10. These same interactions can persist into the solid state as well. For example, aluminum chloride crystallizes from water as a hydrate with formula $AlCl_3{\cdot}6H_2O$. In it the Al^{3+} ion is surrounded by water molecules at the vertices of an octahedron, as illustrated in Figure 12.11. They are held there by ion–dipole attractions.

Ions are also capable of distorting nearby electron clouds, thereby creating dipoles in neighboring particles (like molecules of a solvent, or even other ions). This leads to **ion–induced dipole** attractions, which can be quite strong because the charge on the ion doesn't flicker on and off like the instantaneous charges responsible for ordinary London dispersion forces.

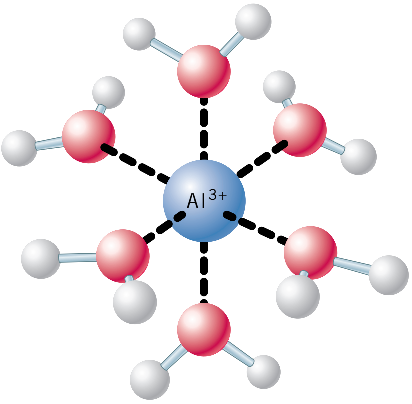


Figure 12.11 | **Ion–dipole attractions hold water molecules in a hydrate.** Water molecules are arranged at the vertices of an octahedron around an aluminum ion in $AlCl_3{\cdot}6H_2O$.

Estimating the Effects of Intermolecular Forces

In this section we have described a number of different types of intermolecular attractive forces and the kinds of substances in which they occur (see the summary in Table 12.3). With this knowledge, you should now be able to make some estimate of the nature and relative strengths of intermolecular attractions if you know the molecular structure of a

TOOLS

Types of intermolecular forces

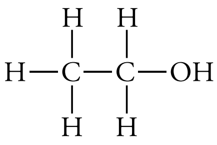
Table 12.3 **Summary of Intermolecular Attractions**

Intermolecular Attraction	Types of Substances that Exhibit Attraction	Strength Relative to a Covalent Bond
London dispersion forces	All atoms, molecules, and ions experience these kinds of attractions. They are present in all substances.	Depends on sizes and shapes of molecules. For large molecules, the cumulative effect of many weak attractions can lead to a large net attraction.
Dipole–dipole attractions	Occur between molecules that have permanent dipoles (i.e., polar molecules).	1–5%
Hydrogen bonding	Occurs when molecules contain N—H, F—H, and O—H bonds.	5–10%
Ion–dipole attractions	Occur when ions interact with polar molecules.	About 10%; depends on ion charge and polarity of molecule.
Ion–induced dipole attractions	Occur when an ion creates a dipole in a neighboring particle, which may be a molecule or another ion.	Variable, depending on the charge on the ion and the polarizability of its neighbor.

substance. This will enable you to understand and sometimes predict how the physical properties of different substances compare. For example, we've already mentioned that boiling point is a property that depends on the strengths of intermolecular attractions. By being able to compare intermolecular forces in different substances, we can sometimes predict how their boiling points compare. This is illustrated in Example 12.1.

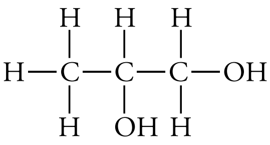
Example 12.1
Using Relative Attractive Forces to Predict Properties

Below are structural formulas of ethanol (ethyl alcohol) and propylene glycol (a compound used as a nontoxic antifreeze). Which of these compounds would be expected to have the higher boiling point?



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

ethanol



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \end{array}$$

propylene glycol

Analysis: We know that boiling points are related to the strengths of intermolecular attractions—the stronger the attractions, the higher the boiling point. Therefore, if we can determine which compound has the stronger intermolecular attractions, we can answer the question. Let's decide which kinds of attractions are present and then try to determine their relative strengths.

Assembling the Tools: The tools we will use are the kinds of intermolecular attractions and their relative strengths and how these interactions affect the boiling points of the liquids.

Solution: We know that both substances will experience London forces, because they are present between *all* molecules. London forces become stronger as molecules become larger, so the London forces should be stronger in propylene glycol.

Looking at the structures, we see that both contain —OH groups (one in ethanol and two in propylene glycol). This means we can expect that there will be hydrogen bonding in both liquids. Because there are more —OH groups per molecule in propylene glycol than in ethanol, we might reasonably expect that there are more opportunities for the ethylene glycol molecules to participate in hydrogen bonding. This would make the hydrogen bonding forces greater in propylene glycol.

Our analysis tells us that both kinds of attractions are stronger in propylene glycol than in ethanol, so propylene glycol should have the higher boiling point.

Is the Answer Reasonable? There's not much we can do to check our answer other than to review the reasoning, which is sound. (We could also check a reference book, where we would find that the boiling point of ethanol is 78.5 °C and the boiling point of propylene glycol is 188.2 °C!)

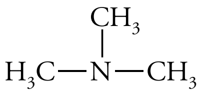
Practice Exercises

12.1 | List the following in order of their boiling points from lowest to highest.
(a) KBr, $CH_3CH_2CH_2CH_2CH_3$, CH_3CH_2OH
(b) $CH_3CH_2NH_2$, $CH_3CH_2{-}O{-}CH_2CH_3$, $HOCH_2CH_2CH_2CH_2OH$
(*Hint:* Determine the type of intermolecular attractive force that is important for each molecule.)

12.2 | Propylamine and trimethylamine have the same molecular formula, C_3H_9N, but quite different structures, as shown below. Which of these substances is expected to have the higher boiling point? Why?

$CH_3{-}CH_2{-}CH_2{-}NH_2$

propylamine



$$\begin{array}{ccccc} & & \mathrm{CH_3} & & \\ & & | & & \\ \mathrm{H_3C} & - & \mathrm{N} & - & \mathrm{CH_3} \end{array}$$

trimethylamine

12.3 | Intermolecular Forces and Properties of Liquids and Solids

Earlier we briefly described some properties of liquids and solids. We continue here with a more in-depth discussion, and we'll start by examining two properties that depend mostly on how tightly packed the molecules are—namely, *compressibility* and *diffusion*. Other properties depend much more on the strengths of intermolecular attractive forces, properties such as *retention of volume or shape, surface tension*, the ability of a liquid to *wet* a surface, the *viscosity* of a liquid, and a solid's or liquid's *tendency to evaporate*.

Properties that Depend on Tightness of Packing

Compressibility

The **compressibility** of a substance is a measure of its ability to be forced into a smaller volume. Gases are highly compressible because the molecules are far apart (Figure 12.12*a*). In a liquid or solid, however, most of the space is taken up by the molecules, and there is very little empty space into which to crowd other molecules (Figure 12.12*b*). As a result, it is very difficult to compress liquids or solids to a smaller volume by applying pressure, so we say that these states of matter are nearly **incompressible**. This is a useful property. When you "step on the brakes" of a car, for example, you rely on the incompressibility of the brake fluid to transmit the pressure you apply with your foot to the brake shoes on the wheels. The incompressibility of liquids is also the foundation of the engineering science of *hydraulics*, which uses fluids to transmit forces that lift or move heavy objects.

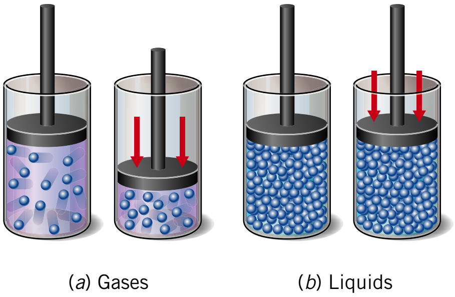


Figure 12.12 | **The compressibility of a gas and a liquid viewed at the molecular level.** (*a*) Gases compress easily because the molecules are far apart. (*b*) Liquids are incompressible because the molecules are packed together.

Diffusion

Diffusion occurs much more rapidly in gases than in liquids, and hardly at all in solids. In gases, molecules diffuse rapidly because they travel relatively long distances between collisions, as illustrated in Figure 12.13. In liquids, however, a given molecule suffers many collisions as it moves about, so it takes longer to move from place to place, making diffusion much slower. Diffusion in solids is almost nonexistent at room temperature because the particles of a solid are held tightly in place. At high temperatures, though, the particles of a solid sometimes have enough kinetic energy to jiggle their way past each other, and diffusion can occur slowly. Such high-temperature, solid-state diffusion is used to make electronic devices such as transistors.

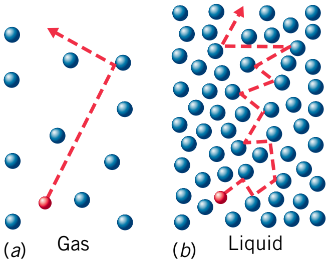


Figure 12.13 | **Diffusion in a gas and a liquid viewed at the molecular level.** (*a*) Diffusion in a gas is rapid because relatively few collisions occur between widely spaced molecules. (*b*) Diffusion in a liquid is slow because of the many collisions between closely spaced particles.

Properties that Depend on Strengths of Intermolecular Attractions

Retention of Volume and Shape

In gases, intermolecular attractions are too weak to prevent the molecules from moving apart to fill an entire vessel, so a gas will conform to the shape and volume of its container, as shown in Figure 12.1. In liquids and solids, however, the attractions are much stronger and are able to hold the particles closely together. As a result, liquids and solids keep the same volume regardless of the size of their container. In a solid, the attractions are even stronger than in a liquid. They hold the particles more or less rigidly in place, so a solid retains its shape when moved from one container to another.

Surface Tension

A property that is especially evident for liquids is *surface tension*, which is related to the tendency of a liquid to seek a shape that yields the minimum surface area. For a given

■ Because of strong hydrogen bonding, the surface tension of water is roughly two to three times larger than the surface tension of any common organic solvent.

volume, the shape with the minimum surface area is a sphere—it's a principle of solid geometry. This is why raindrops tend to be little spheres.

To understand surface tension, we need to examine why molecules would prefer to be within the bulk of a liquid rather than at its surface. In Figure 12.14, we see that a molecule *within* the liquid is surrounded by molecules on all sides, whereas one at the *surface* has neighbors beside and below it, but none above. As a result, a surface molecule is attracted to fewer neighbors than one within the liquid. Now, let's imagine how we might move an interior molecule to one at the surface. We would have to pull away some of the surrounding molecules. Because there are intermolecular attractions, removing neighbors requires work, in which case there is an increase in potential energy involved. Therefore, a molecule at the surface has a higher potential energy than a molecule in the bulk of the liquid.

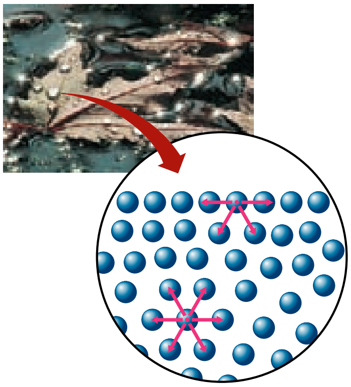


Figure 12.14 | **Surface tension and intermolecular attractions.** In water, as in other liquids, molecules at the surface are surrounded by fewer molecules than those below the surface. As a result, surface molecules experience fewer attractions than molecules within the liquid. *(Pat O'Hara/Stone/Getty Images)*

In general, a system becomes more stable when its potential energy decreases. For a liquid, reducing its surface area (and thereby reducing the number of molecules at the surface) lowers its potential energy. The lowest energy is achieved when the liquid has the smallest surface area possible (namely, a spherical shape). In more accurate terms, then, *the* **surface tension** *of a liquid is proportional to the energy needed to expand its surface area.*

The tendency of a liquid to spontaneously acquire a minimum surface area explains many common observations. For example, surface tension causes the sharp edges of glass tubing to become rounded when the glass is softened in a flame, an operation called "fire polishing." Surface tension is also what allows us to fill a water glass above the rim, giving the surface a rounded appearance (Figure 12.15). The surface behaves as if it has a thin, invisible "skin" that lets the water in the glass pile up, trying to assume a spherical shape. If you push on the surface of a liquid, it resists expansion and pushes back, so the surface "skin" appears to resist penetration. This is what enables certain insects to "walk on water," as illustrated in the photo in the margin on page 539.

Surface tension is a property that varies with the strengths of intermolecular attractions. Liquids with strong intermolecular attractive forces have large differences in potential energy between their interior and surface molecules, and have large surface tensions. Not surprisingly, water's surface tension is among the highest known (with comparisons made at the same temperature); its intermolecular forces are hydrogen bonds, the strongest kind of dipole–dipole attraction. In fact, the surface tension of water is roughly three times that of gasoline, which consists of relatively nonpolar hydrocarbon molecules able to experience only London forces.

Wetting of a Surface by a Liquid

A property we associate with liquids, especially water, is their ability to wet things. **Wetting** is the spreading of a liquid across a surface to form a thin film. Water wets clean glass, such as the windshield of a car, by forming a thin film over the surface of the glass (see Figure 12.16*a*). Water won't wet a greasy windshield, however. On greasy glass, water forms tiny droplets or beads (see Figure 12.16*b*).

For wetting to occur, the intermolecular attractions between the liquid and the surface must be of about the same strength as the attractions within the liquid itself. Such a rough equality exists when water touches clean glass. This is because the glass surface contains lots of oxygen atoms to which water molecules can form hydrogen bonds. As a result, part of the energy needed to expand the water's surface area when wetting occurs is recovered by the formation of hydrogen bonds to the glass surface.

When the glass is coated by a film of oil or grease, the surface exposed to the water drop becomes oil and grease and is now composed of relatively nonpolar molecules (Figure 12.16*b*). These attract other molecules (including water) largely by London forces, which are weak compared with hydrogen bonds. Therefore, the attractions *within* liquid water are much stronger than the attractions *between* water molecules and the greasy surface. The weak water-to-grease London forces can't overcome the hydrogen bonding within liquid water, so the water doesn't spread out; it forms beads, instead.

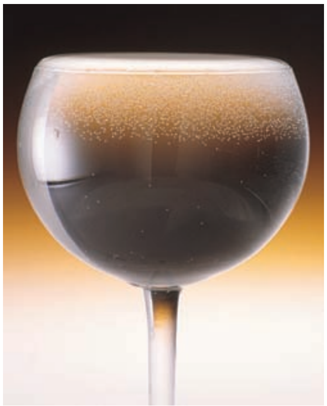
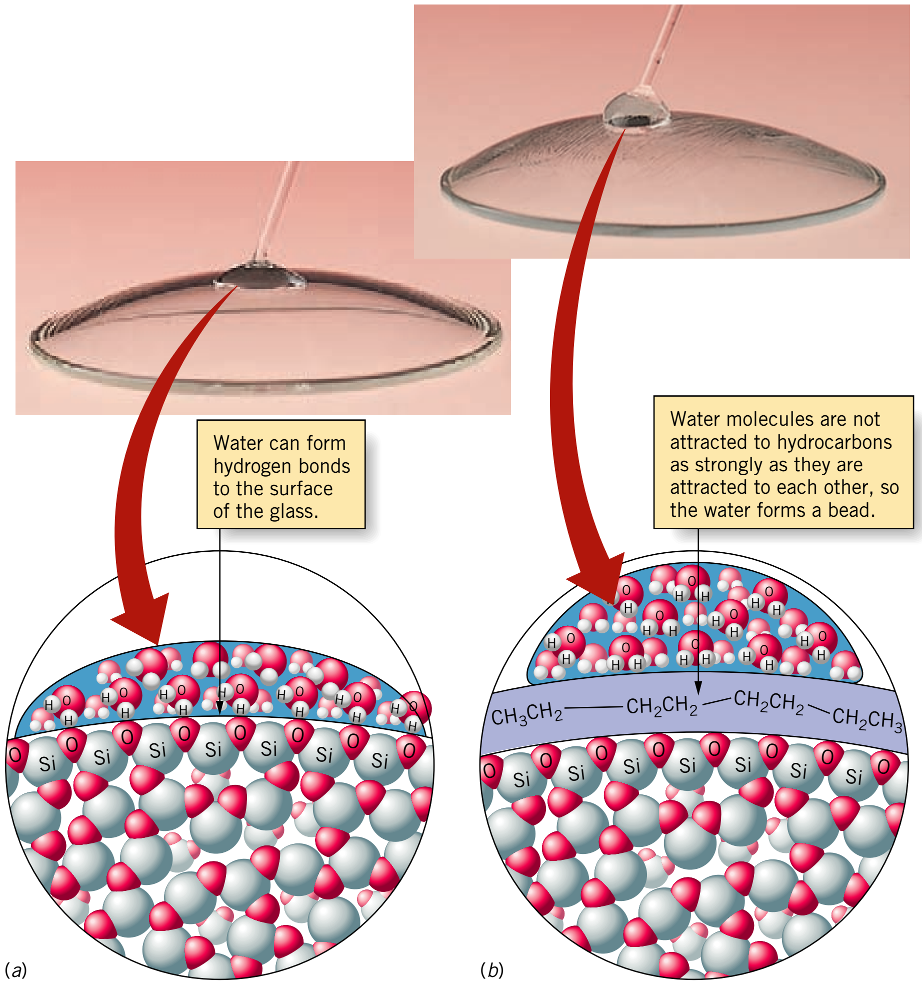


Figure 12.15 | **Surface tension in a liquid.** Surface tension allows a glass to be filled with water above the rim. *(Michael Watson)*



Water can form hydrogen bonds to the surface of the glass.

Water molecules are not attracted to hydrocarbons as strongly as they are attracted to each other, so the water forms a bead.

Figure 12.16 | **Intermolecular attractions affect the ability of water to wet a surface.** (*a*) Water wets a clean glass surface because the surface contains many oxygen atoms to which water molecules can form hydrogen bonds. (*b*) If the surface has a layer of grease, to which water molecules are only weakly attracted, the water doesn't wet it. The water resists spreading and forms a bead instead. *(Michael Watson)*

■ Glass is a vast network of silicon–oxygen bonds.

One of the reasons that detergents are used for such chores as doing laundry or washing floors is that detergents contain chemicals called **surfactants**, which drastically lower the surface tension of water. This makes the water "wetter," which allows the detergent solution to spread more easily across the surface to be cleaned.

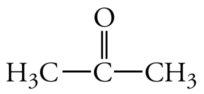
When a liquid has a low surface tension, like gasoline, we know that it has weak intermolecular attractions, and such a liquid easily wets solid surfaces. The weak attractions between the molecules in gasoline, for example, are readily replaced by attractions to almost any surface, so gasoline easily spreads to a thin film. If you've ever spilled a little gasoline, you have experienced firsthand that it doesn't bead.

Viscosity

As everybody knows, syrup flows less readily or is more resistant to flow than water when both are at the same temperature. Flowing is a change in the *form* of the liquid, and such resistance to a change in form is called the liquid's **viscosity**. We say that syrup is more *viscous* than water. The concept of viscosity is not confined to liquids, however, although it is with liquids that the property is most commonly associated. Solid things, even rock, also yield to forces acting to change their shapes, but normally do so only gradually and imperceptibly. Gases also have viscosity, but they respond almost instantly to form-changing forces.

An insect called a *waterstrider*, shown here, is able to walk on water because of the liquid's surface tension, which causes the water to behave as though it has a skin that resists piercing by the insect's legs. *(Hermann Eisenbeiss/Photo Researchers)*

Viscosity has been called the "internal friction" of a material. It is influenced both by intermolecular attractions and by molecular shape and size. For molecules of similar size, we find that as the strengths of the intermolecular attractions increase, so does the viscosity. For example, consider acetone (nail polish remover) and ethylene glycol (automotive antifreeze), each of which contains 10 atoms.



$$\mathrm{H_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

acetone

$$\mathrm{HO{-}CH_2{-}CH_2{-}OH}$$

ethylene glycol

■ If you've ever spilled a little acetone, you know that it flows very easily. In contrast, ethylene glycol has an "oily" thickness to it and flows more slowly.

Ethylene glycol is more viscous than acetone, and their molecular structures reveal why. Acetone contains a polar carbonyl group ($>C{=}O$), so it experiences dipole–dipole attractions as well as London forces. Ethylene glycol, on the other hand, contains two —OH groups, so in addition to London forces, ethylene glycol molecules also participate in hydrogen bonding (a much stronger interaction than ordinary dipole–dipole forces). Strong hydrogen bonding in ethylene glycol makes it more viscous than acetone.

Molecular size and the ability of molecules to tangle with each other is another major factor in determining viscosity. The long, floppy, entangling molecules in heavy machine oil (almost entirely a mixture of long chain, nonpolar hydrocarbons), plus the London forces in the material, give it a viscosity roughly 600 times that of water at 15 °C. Vegetable oils, like the olive oil or corn oil used to prepare salad dressings, consist of molecules that are also large but generally nonpolar. Olive oil is roughly 100 times more viscous than water.

■ As the temperature drops, molecules move more slowly and intermolecular forces become more effective at restraining flow.

Viscosity also depends on temperature; as the temperature decreases, the viscosity increases. When water is cooled from its boiling point to room temperature, for example, its viscosity increases by over a factor of three. The increase in viscosity with cooling is why operators of vehicles use a "light," thin (meaning less viscous) motor oil during subzero weather.

Evaporation, Sublimation, and Intermolecular Attractions

Naphthalene sublimes when heated and the vapor condenses directly to a solid when it encounters a cool surface.

One of the most important physical properties of liquids and solids is their tendency to undergo a change of state from liquid to gas or from solid to gas. For liquids, the change is called **evaporation**. For solids, the change directly to the gaseous state by evaporation without going through the liquid state is called **sublimation**. Solid carbon dioxide is commonly called *dry ice* because it doesn't melt. Instead, at atmospheric pressure it *sublimes,* changing directly to gaseous CO_2. Naphthalene, the ingredient in some brands of moth flakes, is another substance that can sublime and seemingly disappear.

To understand evaporation and sublimation, we have to examine the motions of molecules. In a solid or liquid, molecules are not stationary; they bounce around, colliding with their neighbors. At a given temperature, there is *exactly the same* distribution of kinetic energies in a liquid or a solid as there is in a gas, which means that Figure 7.4 on page 259 applies to liquids and solids, too. This figure tells us that at a given temperature a small fraction of the molecules have very large kinetic energies and therefore very high velocities. When one of these high-velocity molecules is at the surface and is moving outward fast enough, it can escape the attractions of its neighbors and enter the vapor state. We say the molecule has left by evaporation (or sublimation, if the substance is a solid).

Cooling by Evaporation

One of the things we notice about the evaporation of a liquid is that it produces a cooling effect. You've experienced this if you've stepped out of a shower and been chilled by the air. The evaporation of water from your body produced this effect. In fact, our bodies use the evaporation of perspiration to maintain a constant body temperature.

We can see why liquids become cool during evaporation by examining Figure 12.17, which illustrates the kinetic energy distribution in a liquid at a particular temperature.

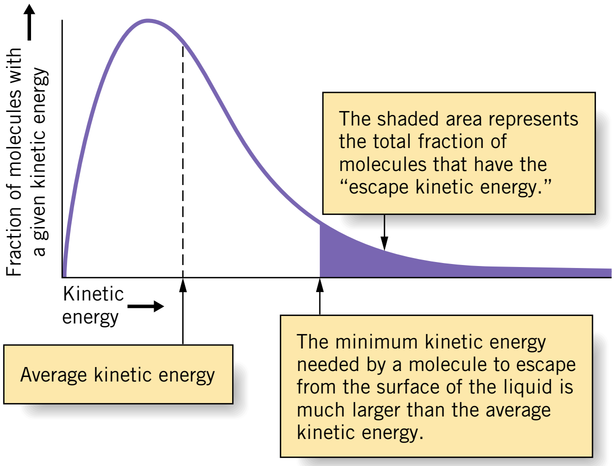


Figure 12.17 | **Cooling of a liquid by evaporation.** Molecules that are able to escape from the liquid have kinetic energies larger than the average. When they leave, the average kinetic energy of the molecules left behind is less, so the temperature is lower.

A marker along the horizontal axis shows the minimum kinetic energy needed by a molecule to escape the attractions of its neighbors. Only molecules with kinetic energies equal to or greater than the minimum can leave the liquid. Others may begin to leave, but before they can escape they slow to a stop and then fall back. Notice in Figure 12.17 that the minimum kinetic energy needed to escape is much larger than the average, which means that when molecules evaporate they carry with them large amounts of kinetic energy. As a result, the average kinetic energy of the molecules left behind decreases. (You might think of this as being similar to removing people taller than 6 feet from a large class of students. When this is done, the average height of those who are left is less.) Because the Kelvin temperature of the remaining liquid is directly proportional to the now lower average kinetic energy, the temperature is lower; in other words, evaporation causes the liquid that remains to be cooler.

Rate of Evaporation

Later in this chapter we will be concerned about the *rate of evaporation* of a liquid. There are several factors that control this. You are probably already aware of one of them—the surface area of the liquid. Because evaporation occurs from the liquid's surface and not from within, it makes sense that as the surface area is increased, more molecules are able to escape and the liquid evaporates more quickly. For liquids having the same surface area, the rate of evaporation depends on two factors—namely, temperature and the strengths of intermolecular attractions. Let's examine each of them separately.

■ To understand how temperature and intermolecular forces affect the rate of evaporation, we must compare evaporation rates from the same size surface area. In this discussion, therefore, "rate of evaporation" means "rate of evaporation *per unit surface area*."

As the temperature increases, so does the evaporation rate. Hot water, as you already know, evaporates faster than cold water. The reason can be seen by studying Figure 12.18, which shows kinetic energy distributions for the *same* liquid at two temperatures. Notice

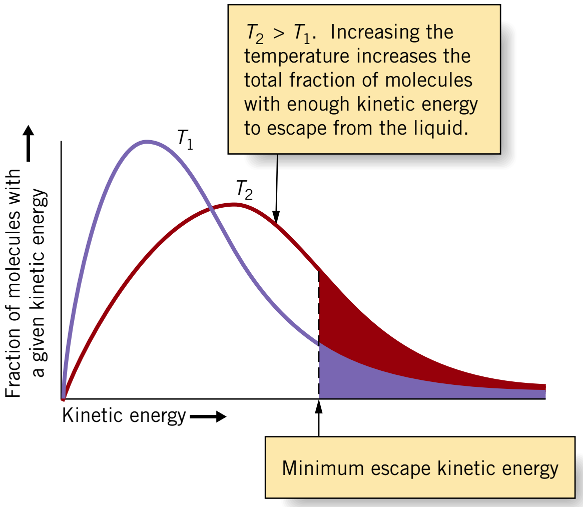


Figure 12.18 | **The effect of increasing the temperature on the rate of evaporation of a liquid.** At the higher temperature, the total fraction of molecules with enough kinetic energy to escape is larger, so the rate of evaporation is larger.

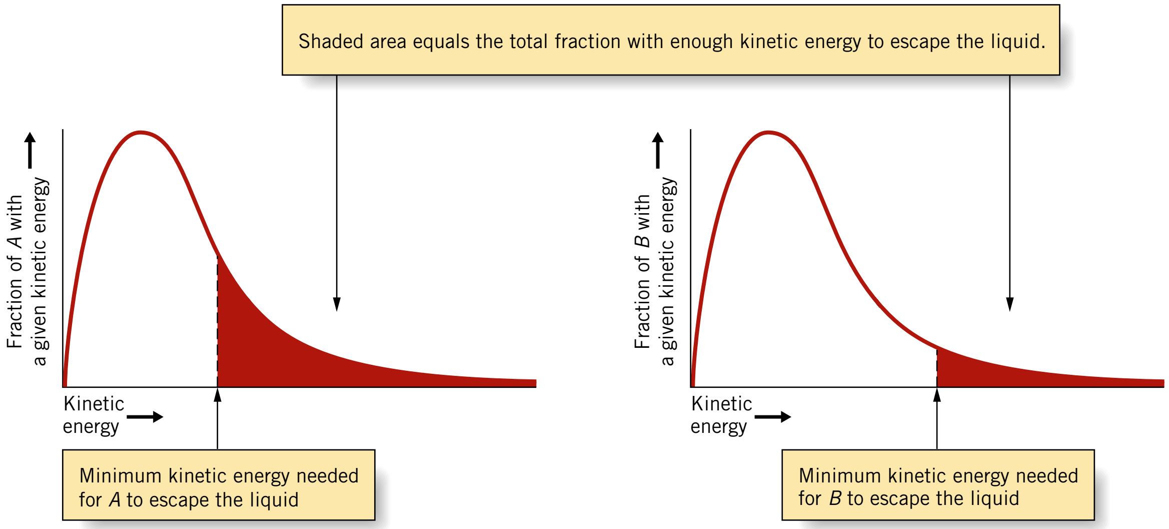


Figure 12.19 | **The kinetic energy distribution in two different liquids, *A* and *B*, at the same temperature.** The minimum kinetic energy required by molecules of *A* to escape is less than for *B* because the intermolecular attractions in *A* are weaker than in *B*. This causes *A* to evaporate faster than *B*.

two important features of the figure. First, the same minimum kinetic energy is needed for the escape of molecules at both temperatures. This minimum is determined by the kinds of attractive forces between the molecules, and is independent of temperature. Second, the shaded area of the curve represents the *total* fraction of molecules having kinetic energies equal to or greater than the minimum. At the higher temperature, the total fraction is larger, which means that at the higher temperature a greater total fraction has the ability to evaporate. As you might expect, when more molecules have the needed energy, more evaporate in a unit of time. Therefore, *the rate of evaporation per unit surface area of a given liquid is greater at a higher temperature.*

TOOLS

Factors that affect the rate of evaporation: temperature and intermolecular forces

The effect of intermolecular attractions on evaporation rate can be seen by studying Figure 12.19. Here we have kinetic energy distributions for two *different* liquids—call them *A* and *B*—both at the same temperature. In liquid *A*, the attractive forces are weak; they might be of the London type, for example. As we see, the minimum kinetic energy needed by *A* molecules to escape is not very large because they are not attracted very strongly to each other. In liquid *B*, the intermolecular attractive forces are much stronger; they might be hydrogen bonds, for instance. Molecules of *B*, therefore, are held more tightly to each other at the liquid's surface and must have a higher kinetic energy to evaporate. As you can see from the figure, the total fraction of molecules with enough energy to evaporate is greater for *A* than for *B*, which means that *A* evaporates faster than *B*. In general, then, *the weaker the intermolecular attractive forces, the faster is the rate of evaporation at a given temperature.* You are probably also aware of this phenomenon. At room temperature, for example, nail polish remover [acetone, $(CH_3)_2CO$], whose molecules experience weak dipole–dipole and London forces of attraction, evaporates faster than water, whose molecules feel the effects of much stronger hydrogen bonds.

12.4 | Changes of State and Dynamic Equilibria

A **change of state** occurs when a substance is transformed from one physical state to another (Figure 12.20). The evaporation of a liquid into a gas and the sublimation of a solid into a gas are two examples. Others are the melting, or **fusion**, of a solid such as ice and the

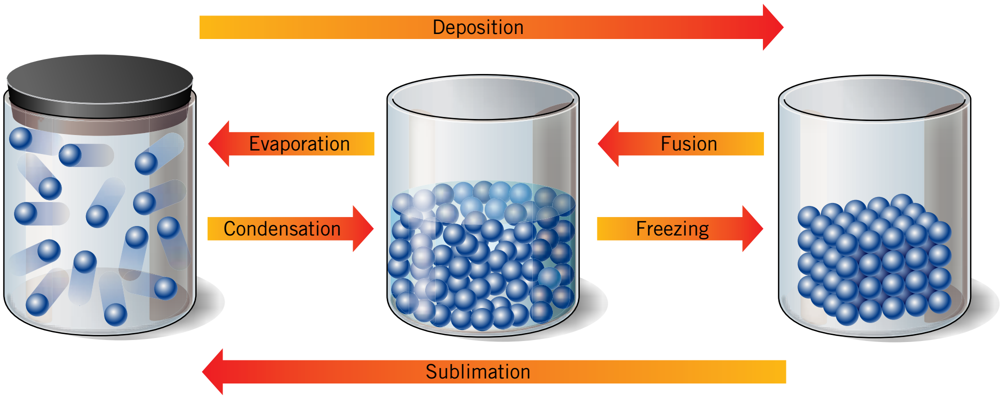

Deposition
Evaporation
Condensation
Fusion
Freezing
Sublimation

Figure 12.20 | **Changes of state between gases, solids, and liquids.**

freezing of a liquid such as water. Finally, a gas can become a solid in a process called **deposition** or a liquid through **condensation**.

One of the important features about changes of state is that, at any particular temperature, they always tend toward a condition of *dynamic equilibrium.* We introduced the concept of dynamic equilibrium on page 170 with an example of a system at chemical equilibrium. The same general principles apply to a physical equilibrium, such as that between a liquid and its vapor. Let's see how such an equilibrium is established.

When a liquid is placed in an empty container, it immediately begins to evaporate and molecules of the substance begin to collect in the space above the liquid (see Figure 12.21*a*). As they fly around in the vapor, the molecules collide with each other, with the walls of the container, and with the surface of the liquid itself. Those that strike the liquid's surface tend to stick because their kinetic energies become scattered among the surface molecules, thus condensing from a gas to a liquid.

■ In chemistry (unless otherwise indicated), when we use the term *equilibrium*, we always mean *dynamic equilibrium.*

Fusion means melting. The thin metal band in an electrical fuse becomes hot as electricity passes through it. It protects a circuit by melting if too much current is drawn. On the right we see a fuse that has done its job. *(Michael Watson)*

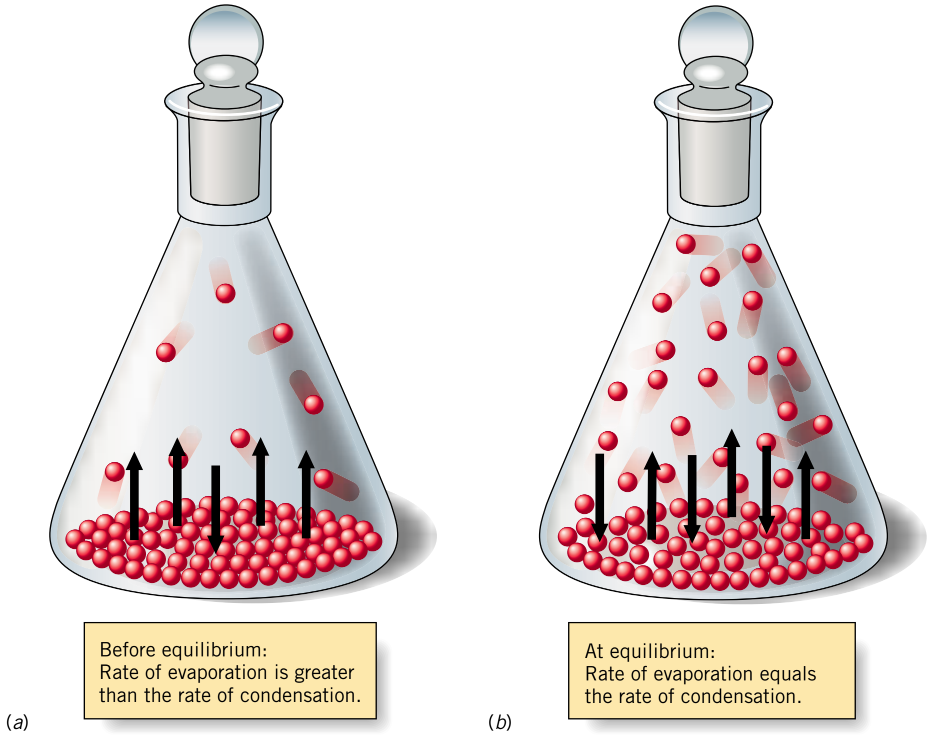

Before equilibrium:
Rate of evaporation is greater
than the rate of condensation.
(*a*)
At equilibrium:
Rate of evaporation equals
the rate of condensation.
(*b*)

Figure 12.21 | **The evaporation of a liquid into a sealed container.** (*a*) The liquid has just begun to evaporate into the container. The rate of evaporation is greater than the rate of condensation. (*b*) A dynamic equilibrium is reached when the rate of evaporation equals the rate of condensation. In a given time period, the number of molecules entering the vapor equals the number that leave, so there is no net change in the number of gaseous molecules.

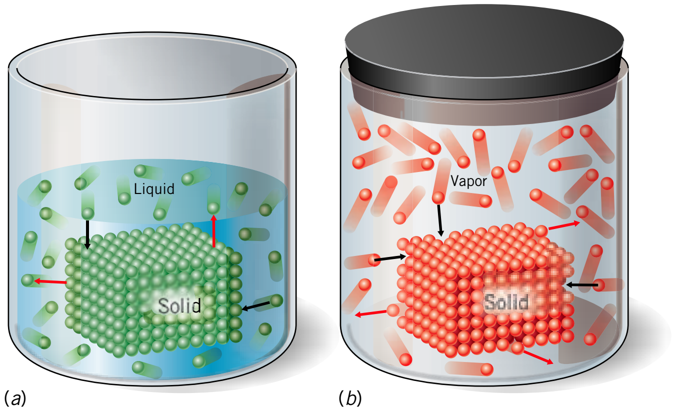


Figure 12.22 | **Solid–liquid and solid–vapor equilibria.** (*a*) As long as no heat is added or removed, melting (red arrows) and freezing (black arrows) occur at equal rates and the number of particles in the solid remains constant. (*b*) Equilibrium is established when molecules sublime from the solid at the same rate as they deposit on the solid from the vapor.

Initially, when the liquid is first introduced into the container, the rate of evaporation is high, but the rate of condensation is very low because there are few molecules in the vapor state. As vapor molecules accumulate, the rate of condensation increases. This continues until the rate at which molecules are condensing becomes equal to the rate at which they are evaporating (Figure 12.21*b*). From that moment on, the number of molecules in the vapor will remain constant, because over a given period of time the number that enters the vapor is the same as the number that leaves. At this point we have a condition of *dynamic equilibrium,* one in which two opposing effects, evaporation and condensation, are occurring at equal rates.

■ A vapor–liquid equilibrium is possible only in a closed container. When the container is open, vapor molecules drift away and the liquid might completely evaporate.

Similar equilibria are also reached in melting and sublimation. At a temperature called the **melting point**, a solid begins to change to a liquid as heat is added. At this temperature a dynamic equilibrium can exist between molecules in the solid and those in the liquid. Molecules leave the solid and enter the liquid at the same rate as molecules leave the liquid and join the solid (Figure 12.22*a*). As long as no heat is added or removed from such a solid–liquid equilibrium mixture, melting and freezing occur at equal rates. For sublimation, the situation is exactly the same as in the evaporation of a liquid into a sealed container (see Figure 12.22*b*). After a few moments, the rates of sublimation and deposition become the same and equilibrium is established.

12.5 | Vapor Pressures of Liquids and Solids

When a liquid evaporates, the molecules that enter the vapor exert a pressure called the **vapor pressure**. From the very moment a liquid begins to evaporate into the vapor space above it, there is a vapor pressure. If the evaporation is taking place inside a sealed container, this pressure grows until finally equilibrium is reached. Once the rates of evaporation and condensation become equal, the concentration of molecules in the vapor remains constant and the vapor exerts a constant pressure. This final pressure is called the **equilibrium vapor pressure of a liquid.** In general, when we refer to the *vapor pressure*, we really mean the equilibrium vapor pressure.

Factors that Determine the Equilibrium Vapor Pressure

Figure 12.23 shows plots of equilibrium vapor pressure versus temperature for a few liquids. From these graphs we see that both a liquid's temperature and its chemical composition are the major factors affecting its vapor pressure. Once we have selected a particular liquid, however, only the temperature matters. The reason is that the vapor pressure of a given liquid is a function solely of its rate of evaporation *per unit area of the liquid's surface.* When this rate is large, a large concentration of molecules in the vapor state is necessary to establish equilibrium, which is another way of saying that the vapor pressure is relatively high when the evaporation rate is high. As the temperature of a given liquid increases, so does its rate of evaporation and so does its equilibrium vapor pressure.

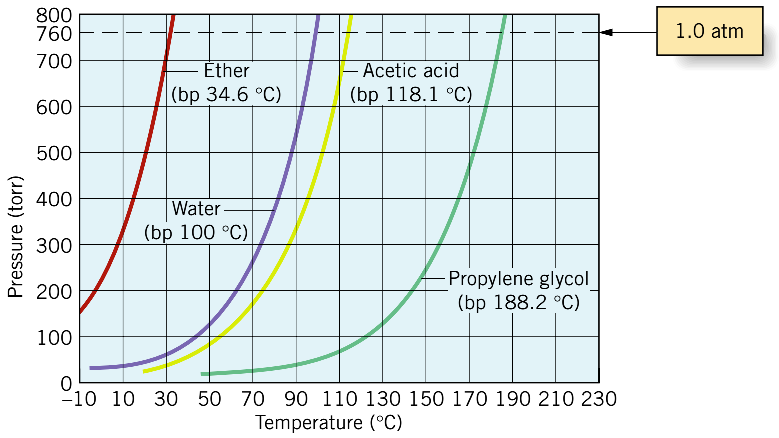


Figure 12.23 | **The variation of vapor pressure with temperature for some common liquids.**

As chemical composition changes in going from one liquid to another, the strengths of intermolecular attractions change. If the attractions increase, the rates of evaporation at a given temperature decrease, and the vapor pressures decrease. These data on relative vapor pressures tell us that, of the four liquids in Figure 12.23, intermolecular attractions are strongest in propylene glycol, next strongest in acetic acid, third strongest in water, and weakest in ether. Thus, *we can use vapor pressures as indications of relative strengths of the attractive forces in liquids.*

■ A liquid with a high vapor pressure at a given temperature is said to be *volatile*.

We can then say that two factors affect the equilibrium vapor pressure. The first is temperature: for a given substance, as the temperature increases, the vapor pressure increases. The second is the intermolecular forces: when comparing two substances, the stronger the intermolecular forces, the lower the vapor pressure.

TOOLS

Factors that affect vapor pressure

Factors that Do Not Affect the Equilibrium Vapor Pressure

An important fact about vapor pressure is that *its magnitude doesn't depend on the* total *surface area of the liquid, or on the volume of the liquid in the container, or on the volume of the container itself, just as long as some liquid remains when equilibrium is reached.* The reason is because none of these factors affects the rate of evaporation *per unit surface area*.

Increasing the *total* surface area does increase the *total* rate of evaporation, but the larger area is also available for condensation; as a result, the rate at which molecules return to the liquid also increases. The rates of both evaporation and condensation are thus affected equally, and no change occurs to the equilibrium vapor pressure.

Adding more liquid to the container can't affect the equilibrium either because evaporation occurs from the *surface*. Having more molecules in the bulk of the liquid does not change what is going on at the surface.

To understand why the vapor pressure doesn't depend on the *size* of the vapor space, consider a liquid in equilibrium with its vapor in a cylinder with a movable piston, as illustrated in Figure 12.24*a*. Withdrawing the piston (Figure 12.24*b*) increases the volume of the vapor space; as the vapor expands, the pressure it exerts becomes less, so there's a momentary drop in the pressure. The molecules of the vapor, being more spread out now, no longer strike the surface as frequently, so the rate of condensation has also decreased. The rate of evaporation hasn't changed, however, so for a moment the system is not at equilibrium and the substance is evaporating faster than it is condensing (Figure 12.24*b*). This condition prevails, changing more liquid into vapor, until the concentration of molecules in the vapor has risen enough to make the condensation rate equal again to the evaporation rate (Figure 12.24*c*). At this point, the vapor pressure has returned to its original value. Therefore, the net result of expanding the space above the liquid is to change more liquid into vapor, but it does not affect the equilibrium vapor pressure. Similarly, we expect that reducing the volume of the vapor space above the liquid will also not affect the equilibrium vapor pressure, either.

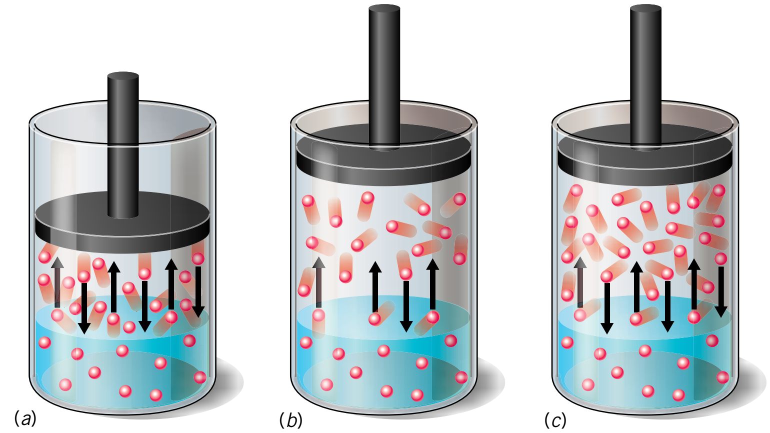


Figure 12.24 | **The effect of a volume change on the vapor pressure of a liquid.** (*a*) Equilibrium exists between liquid and vapor. (*b*) The volume is increased, which upsets the equilibrium and causes the pressure to drop. The rate of condensation is now less than the rate of evaporation, which hasn't changed. (*c*) After more liquid has evaporated, equilibrium is restored and the vapor pressure has returned to its initial value.

Practice Exercises

12.3 | Considering Figure 12.24, in which direction should the piston be moved to decrease the number of molecules in the gas phase? (*Hint:* Consider what must happen to re-establish equilibrium after the piston is moved.)

12.4 | Suppose a liquid is in equilibrium with its vapor in a piston–cylinder apparatus like that in Figure 12.24. If the piston is pushed in a short way and the system is allowed to return to equilibrium, what will have happened to the *total number* of molecules in both the liquid and the vapor?

12.5 | What could be done to the system in order to decrease the number of molecules in the vapor above a liquid while keeping the volume of the vapor space the same?

Vapor Pressures of Solids

Solids have vapor pressures just as liquids do. In a crystal, the particles are constantly jiggling around, bumping into their neighbors. At a given temperature there is a distribution of kinetic energies, so some particles at the surface have large enough kinetic energies to break away from their neighbors and enter the vapor state. When particles in the vapor collide with the crystal, they can be recaptured, so condensation can occur, too. Eventually, the concentration of particles in the vapor reaches a point where the rate of sublimation equals the rate of condensation, and a dynamic equilibrium is established. The pressure of the vapor that is in equilibrium with a solid is called the **equilibrium vapor pressure of a solid.** As with liquids, this equilibrium vapor pressure is usually referred to simply as the vapor pressure. Like that of a liquid, the vapor pressure of a solid is determined by the strengths of the attractive forces between the particles and by the temperature.

■ In many solids, such as NaCl, the attractive forces are so strong that virtually no particles have enough kinetic energy to escape at room temperature, so essentially no evaporation occurs. Their vapor pressures at room temperature are virtually zero.

12.6 | Boiling Points of Liquids

If you were asked to check whether a pot of water was boiling, what would you look for? The answer, of course, is *bubbles*. When a liquid boils, large bubbles usually form at many places on the inner surface of the container and rise to the top. If you were to place a thermometer into the boiling water, you would find that the temperature remains constant, regardless of how you adjust the flame under the pot. A hotter flame just makes the water bubble faster, but it doesn't raise the temperature. *Any pure liquid remains at a constant temperature while it is boiling,* a temperature that's called the liquid's **boiling point**.

If you measure the boiling point of water in Los Angeles, New York, or any place else that is nearly at sea level, your thermometer will read 100 °C or very close to it. However, if you try this experiment in Denver, Colorado, you will find that water boils at about 95 °C. Denver, at a mile above sea level, has a lower atmospheric pressure. Thus, we find that the boiling point depends on the atmospheric pressure.

■ On the top of Mt. Everest, the world's tallest peak, water boils at only 69 °C.

These observations raise some interesting questions. Why do liquids boil? And why does the boiling point depend on the pressure of the atmosphere? The answers become apparent when we realize that inside the bubbles of a boiling liquid is the *liquid's vapor*, not air. When water boils, the bubbles contain water vapor (steam); when alcohol boils, the bubbles contain alcohol vapor. As a bubble grows, liquid evaporates into it, and the pressure of the vapor pushes the liquid aside, making the size of the bubble increase (see Figure 12.25). Opposing the bubble's internal vapor pressure, however, is the pressure of the atmosphere pushing down on the top of the liquid, attempting to collapse the bubble. The only way the bubble can exist and grow is for the vapor pressure within it to equal (maybe just slightly exceed) the pressure exerted by the atmosphere. In other words, bubbles of vapor cannot even form until the temperature of the liquid rises to a point at which the liquid's vapor pressure equals the atmospheric pressure. Thus, in scientific terms, the **boiling point** is defined as *the temperature at which the vapor pressure of the liquid is equal to the prevailing atmospheric pressure.*

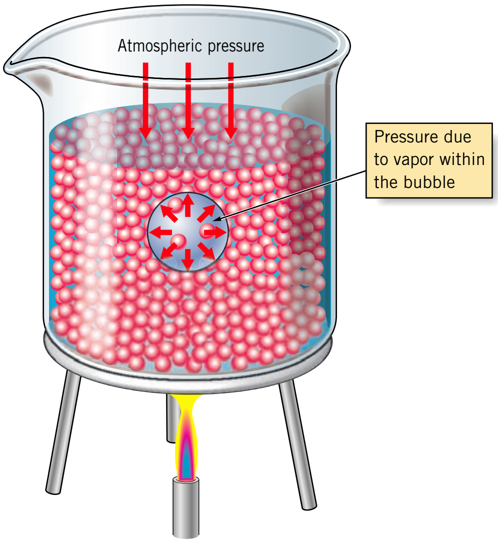

Atmospheric pressure
Pressure due to vapor within the bubble

Figure 12.25 | **A liquid at its boiling point.** The pressure of the vapor within a bubble in a boiling liquid pushes the liquid aside against the opposing pressure of the atmosphere. Bubbles can't form unless the vapor pressure of the liquid is at least equal to the pressure of the atmosphere.

Now we can understand why water boils at a lower temperature in Denver than it does in New York City. Because the atmospheric pressure is lower in Denver, the water there doesn't have to be heated to as high a temperature to make its vapor pressure equal to the atmospheric pressure. The lower temperature of boiling water at places with high altitudes, like Denver, makes it necessary to cook foods longer. At the other extreme, a pressure cooker is a device that increases the pressure over the boiling water and thereby raises the boiling point. At the higher temperature, foods cook more quickly.

To make it possible to compare the boiling points of different liquids, chemists have chosen 1 atm as the reference pressure. The boiling point of a liquid at 1 atm is called its **normal boiling point.**[2] (If a boiling point is reported without also mentioning the pressure at which it was measured, we assume it to be the normal boiling point.) Notice in Figure 12.23, page 545, that we can find the normal boiling points of ether, water, acetic acid, and propylene glycol by noting the temperatures at which their vapor pressure curves cross the 1-atm pressure line.

Boiling Points and Intermolecular Attractions

TOOLS

Boiling points and intermolecular forces

Earlier we mentioned that the boiling point is a property whose value depends on the strengths of the intermolecular attractions in a liquid. When the attractive forces are strong, the liquid has a low vapor pressure at a given temperature, so it must be heated to a high temperature to bring its vapor pressure up to atmospheric pressure. High boiling points, therefore, result from strong intermolecular attractions, so we often use normal boiling point data to assess relative intermolecular attractions among different liquids. (In fact, we did this in solving Example 12.1.)

The effects of intermolecular attractions on boiling point are easily seen by examining Figure 12.26, which gives the plots of the boiling points versus period numbers for some families of binary hydrogen compounds. Notice, first, the gradual increase in boiling point for the hydrogen compounds of the Group 4A elements (CH_4 through GeH_4). These compounds are composed of nonpolar tetrahedral molecules. The boiling points increase from CH_4 to GeH_4 simply because the molecules become larger and their electron clouds become more polarizable, which leads to an increase in the strengths of the London forces.

When we look at the hydrogen compounds of the other nonmetals, we find the same trend from Period 3 through Period 5. Thus, for three compounds of the Group 5A series, PH_3, AsH_3, and SbH_3, there is a gradual increase in boiling point, corresponding again to the increasing strengths of London forces. Similar increases occur for the three Group 6A

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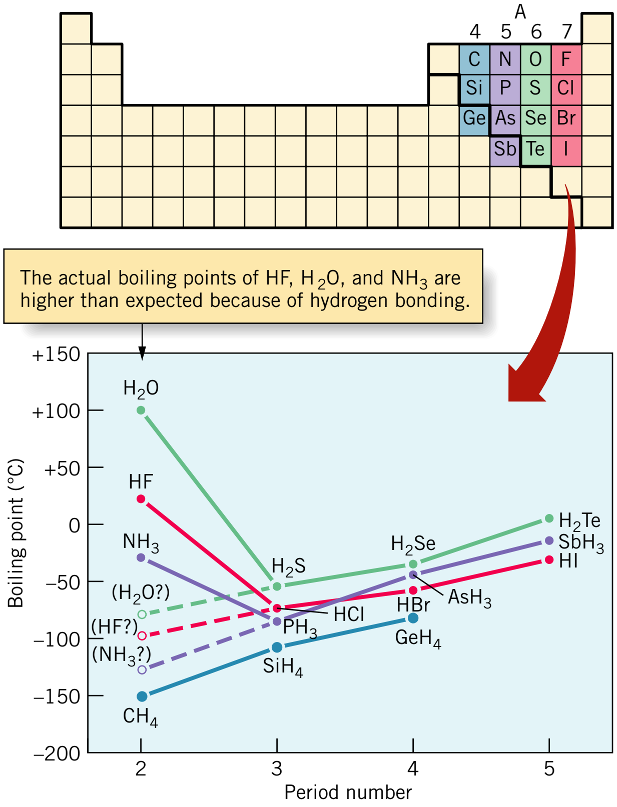
[2] The *standard boiling point* is the boiling point at 1 bar; the difference between the standard boiling point and the normal boiling point is negligible unless extremely precise measurements are being made.

Figure 12.26 | **The effects of intermolecular attractions on the boiling point.** The boiling points of the hydrogen compounds of the elements of Groups 4A, 5A, 6A, and 7A of the periodic table.



The actual boiling points of HF, H_2O, and NH_3 are higher than expected because of hydrogen bonding.

compounds (H_2S, H_2Se, and H_2Te) and for the three Group 7A compounds (HCl, HBr, and HI). Significantly, however, the Period 2 members of each of these series (NH_3, H_2O, and HF) have much higher boiling points than might otherwise be expected. The reason is that each is involved in hydrogen bonding, which is a much stronger attraction than dipole–dipole forces.

One of the most interesting and far-reaching consequences of hydrogen bonding is that it causes water to be a liquid, rather than a gas, at temperatures near 25 °C. If it were not for hydrogen bonding, water would have a boiling point somewhere near −80 °C and could not exist as a liquid except at still lower temperatures. At such low temperatures it is unlikely that life as we know it could have developed.

Practice Exercises

12.6 | The Dead Sea is approximately 1300 ft below sea level and its barometric pressure is approximately 830 torr. Will the boiling point of water be elevated from 100 °C by (a) less than 10 °C, (b) 10 °C to 25 °C, (c) 25 °C to 50 °C, or (d) above 50 °C? (*Hint:* Extrapolate from Figure 12.23.)

12.7 | The atmospheric pressure at the summit of Mt. McKinley in Denali National Park in Alaska, 3.85 miles above sea level, is about 330 torr. Use Figure 12.23 to estimate the boiling point of water at the top of this mountain.

12.7 | Energy and Changes of State

When a liquid or solid evaporates or a solid melts, there are increases in the distances between the particles of the substance. Particles that normally attract each other are forced apart, increasing their potential energies. Such energy changes affect our daily lives in many ways, especially the energy changes associated with the changes in state of water, changes that even control the weather on our planet. To study these energy changes, let's begin by examining how the temperature of a substance varies as it is heated.

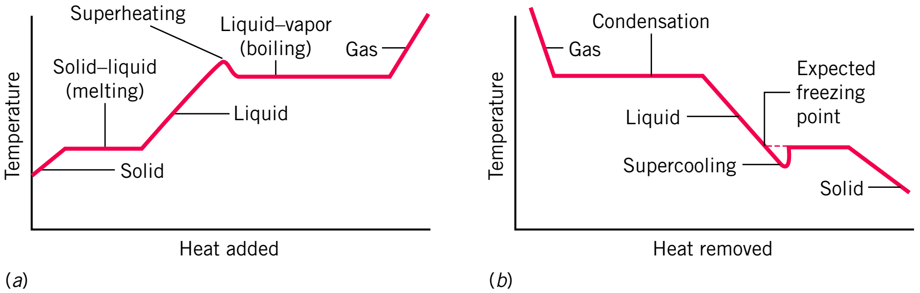


Figure 12.27 | **Heating and cooling curves.** (*a*) A heating curve observed when heat is added to a substance at a constant rate. Superheating is shown as continued heating past the boiling point. (*b*) A cooling curve observed when heat is removed from a substance at a constant rate. Supercooling is seen here as the temperature of the liquid dips below its freezing point. Once a tiny crystal forms, the temperature rises to the freezing point.

Heating Curves and Cooling Curves

Figure 12.27*a* illustrates the way the temperature of a substance changes as we add heat to it *at a constant rate*, starting with the solid and finishing with the gaseous state of the substance. The graph is sometimes called a **heating curve** for the substance.

First, let's look at the portions of the graph that slope upward. These occur where we are increasing the temperature of the solid, liquid, and gas phases. Because temperature is related to average kinetic energy, nearly all of the heat we add in these regions of the heating curve goes to increasing the average kinetic energies of the particles. In other words, the added heat makes the particles go faster and collide with each other with more force. In addition, the slope of the rising portions have units of °C per joule. This is the reciprocal of the heat capacity, meaning that the greater the slope, the lower the heat capacity. Gases have lower heat capacities than liquids and therefore the heating of the gas phase has the largest slope.

■ When a solid or liquid is heated, the volume expands only slightly, so there are only small changes in the average distance between the particles. This means that very small changes in potential energy take place, so almost all of the heat added goes to increasing the kinetic energy.

In those portions of the heating curve where the temperature remains constant, the average kinetic energy of the particles is not changing. This means that all of the heat being added must go to increase the *potential energies* of the particles. During melting, the particles held rigidly in the solid begin to separate slightly as they form the mobile liquid phase. The potential energy increase accompanying this process equals the amount of heat input during the melting process. During boiling, there is an even greater increase in the distance between the molecules. Here they go from the relatively tight packing in the liquid to the widely spaced distribution of molecules in the gas. This gives rise to an even larger increase in the potential energy, which we see as a longer flat region on the heating curve during the boiling of the liquid.

The opposite of a heating curve is a **cooling curve** (see Figure 12.27*b*). Here we start with a gas and gradually cool it—that is, remove heat from it at a constant rate—until we have reached a solid.

Superheating and Supercooling

Looking at Figure 12.27 again we notice two unusual features, one on each curve. There is a small "blip" on the heating curve near the transition from the liquid to a gas. A similar feature occurs when a liquid is cooled to a solid. These "blips" represent the phenomena of superheating and supercooling. **Superheating** occurs when the liquid is heated above the boiling point without boiling. If disturbed, a superheated liquid will erupt with a shower of vapor and liquid. Many people have discovered this effect when heating their favorite beverage in a microwave oven. When cooling a liquid it is possible to decrease the temperature below the freezing point without solidification occurring. Once again, if the supercooled solution is disturbed, very rapid crystallization occurs.

■ The supercooling of a vapor is also possible. The condensation of supercooled water vapor onto solid surfaces leads to dew in warm weather and frost in freezing weather.

Molar Heats of Fusion, Vaporization, and Sublimation

Because phase changes occur at constant temperature and pressure, the potential energy changes associated with melting and vaporization can be expressed as enthalpy changes. Usually, enthalpy changes are expressed on a "per mole" basis and are given special names to identify the kind of change involved. For example, using the word fusion instead of

Enthalpy changes during phase changes

"melting," the **molar heat of fusion,** ΔH_{fusion}, is the heat absorbed by one mole of a solid when it melts to give a liquid at the same temperature and pressure. Similarly, the **molar heat of vaporization,** $\Delta H_{\text{vaporization}}$, is the heat absorbed when one mole of a liquid is changed to one mole of vapor at a constant temperature and pressure. Finally, the **molar heat of sublimation,** $\Delta H_{\text{sublimation}}$, is the heat absorbed by one mole of a solid when it sublimes to give one mole of vapor, once again at a constant temperature and pressure. The values of ΔH for fusion, vaporization, and sublimation are all positive because the phase change in each case is endothermic, being accompanied by a net increase in potential energy.

■ These are also called *enthalpies* of fusion, vaporization, and sublimation.

In order to calculate the amount of heat required to melt a specific amount of a substance, we can multiply the moles of the substance by the molar heat of fusion:

Heat of fusion

$$q = n \times \Delta H_{\text{fusion}} \tag{12.1}$$

in which q is the heat required and n is the number of moles. This equation can also be used to determine the heat required for the process of sublimation or vaporization by substituting $\Delta H_{\text{sublimation}}$ or $\Delta H_{\text{vaporization}}$ for ΔH_{fusion}, respectively.

Examples of the influence of these energy changes on our daily lives abound. For example, you've added ice to a drink to keep it cool, because as the ice melts, it absorbs heat (its heat of fusion). Your body uses the heat of vaporization of water to cool itself through the evaporation of perspiration. During the summer, ice cream trucks carry dry ice because the sublimation of CO_2 absorbs heat and keeps the ice cream cold. And perhaps most important, weather on our planet is driven by the heat of vaporization of water, which converts solar energy into the energy of winds and storms. For example, large storms over oceans, such as hurricanes, rely on a continual supply of warm, moist air produced by the rapid evaporation of water from tropical waters. Continual condensation in the high clouds forms rain and supplies the energy needed to feed the storm's winds.

The solidification of a liquid to a crystal, the condensation of a gas to a liquid, or the deposition of a gas as a solid are simply the reverse of fusion, vaporization, and sublimation processes, respectively. Therefore, the heat of crystallization is equal to the heat of fusion but it has the opposite numerical sign. Similarly, the heats of condensation and deposition have the opposite signs of their counterparts.

Since heat is released when liquids solidify or when gases become solids or liquids, that heat can be put to practical use. For example, refrigerators work by condensing the refrigerant gas; this process releases heat. When the liquid vaporizes in the reverse process, it absorbs heat, the temperature drops, and the refrigerator is cooled. Similarly, meteorologists can often use the "dew point" of the atmosphere to predict overnight low temperatures. The dew point is the temperature at which moisture in the air begins to condense. If the nighttime temperature decreases to the dew point, the heat released by the condensation of water keeps the temperature from falling much further.

Example 12.2

Calculating the Amount of Heat Required during Changes of State

Liquid sodium metal is used as heat transfer material to cool nuclear reactors. How much heat is required to heat 75.0 g of sodium from 25.0 °C to 515.0 °C? The melting point of sodium is 97.8 °C; the specific heat of solid sodium is 1.23 J/g °C; the molar heat of fusion of sodium is 2.60 kJ/mol; and the specific heat of liquid sodium is 1.38 J/g °C. We will assume that the specific heats do not change with temperature.

■ **Analysis:** We are being asked to calculate the amount of heat that will be required to (1) heat the solid to the melting point, (2) melt the solid, and (3) heat the resulting liquid. We are given the amount of sodium and the specific heats of the solid and liquid sodium, in addition to the heat of fusion of sodium. After calculating the different heats, we will add them together to determine the total heat required for the process.

■ **Assembling the Tools:** Using Equation 7.7, $q = ms\,\Delta t$, the amount of heat, q, required to heat the solid and the liquid can be determined from the mass, m, the specific heat of the substance, s, and the change in temperature, Δt. For the process of melting the solid, we will use Equation 12.1, $q = n \times \Delta H_{\text{fusion}}$, in which ΔH_{fusion} is the heat of fusion of sodium.

Solution: Let us start at 25.0 °C to calculate the amount of heat required to heat the sodium to its melting point of 97.8 °C.

$$\begin{aligned} q_1 &= ms\ \Delta t = 75.0\,\cancel{\text{g}} \times 1.23\ \text{J}\ \cancel{\text{g}^{-1}}\ \cancel{{}^\circ\text{C}^{-1}} \times (97.8\ \cancel{{}^\circ\text{C}} - 25.0\ \cancel{{}^\circ\text{C}}) \\ &= 6716\ \text{J} \end{aligned}$$

The next step is melting the sodium at 97.8 °C, and we will use Equation 12.1 to calculate this amount of heat.

$$q_2 = n \times \Delta H_{\text{fusion}}$$

Before proceeding, we need to look at the units for ΔH_{fusion}, which are kJ/mol. The first thing to note is that we are given a mass of sodium, so we need to convert that to moles. Second, the energy units are in kJ but the energy units for heating the solid sodium are in J, so we have to convert them to J.

$$n = 75.0\ \cancel{\text{g Na}} \times \frac{1\ \text{mol Na}}{22.99\ \cancel{\text{g Na}}} = 3.262\ \text{mol Na}$$

$$q_2 = n \times \Delta H_{\text{fusion}} = 3.262\ \cancel{\text{mol Na}} \times \frac{2.60\ \cancel{\text{kJ}}}{\cancel{\text{mol Na}}} \times \frac{1000\ \text{J}}{1\ \cancel{\text{kJ}}}$$

$$q_2 = 8481\ \text{J}$$

The final step in the process is heating the liquid sodium from 97.8 °C to 515.0 °C, so we can calculate the heat absorbed using the same equation as we did in the first step:

$$\begin{aligned} q_3 &= ms\ \Delta t = 75.0\,\cancel{\text{g}} \times 1.38\ \text{J}\ \cancel{\text{g}^{-1}}\ \cancel{{}^\circ\text{C}^{-1}} \times (515.0\ \cancel{{}^\circ\text{C}} - 97.8\ \cancel{{}^\circ\text{C}}) \\ &= 43{,}180\ \text{J} \end{aligned}$$

We add the three heats together to get the total heat:

$$\begin{aligned} q_{\text{total}} &= q_1 + q_2 + q_3 \\ q_{\text{total}} &= 6716\ \text{J} + 8481\ \text{J} + 43{,}180\ \text{J} = 58{,}400\ \text{J} \end{aligned}$$

Is the Answer Reasonable? Since this question has a number of calculations, it would be a good idea to estimate the answer and see whether we are in the ball park. The specific heats for the solid and liquid sodium are approximately 1 J/g, the mass is approximately 100 g, and the change in temperature is about 500 °C, so the heat, q, would be about (1 J/g) × (100 g) × (500 °C) = 50,000 J. We have about 3 mol of sodium, 75 g Na/(1 mol Na/23 g), and the ΔH_{fusion} is about 3000 J/mol, so the heat required to melt the sodium is (3 mol Na) × (3000 J/mol) = 9000 J. Adding these two heats together we get 59,000 J, which is about what we calculated above, indicating that our answer is correct.

Practice Exercises

12.8 | Benzene has a boiling point of 80.1 °C, and a specific heat capacity of 1.8 J/g °C in the liquid phase and 1.92 J/g °C in the gas phase. The $\Delta H_{\text{vaporization}}$ of benzene is 30.77 kJ/mol. How much heat is released when 55 g of benzene in the gas phase is cooled from 105.0 °C to 25.0 °C? (*Hint:* The benzene is cooling from the gas to the liquid, so three steps are needed to solve this problem.)

12.9 | Steam can cause more severe burns than water, even if both are at the same temperature. Calculate the amount of heat released from 10 g of steam at 100.0 °C as it cools to 37 °C (body temperature), and the amount of heat released from 10 g of water at 100.0 °C as it cools to 37 °C. The $\Delta H_{\text{vaporization}}$ of water is 43.9 kJ mol^{-1} and the specific heat of water is 4.184 J g^{-1} °C^{-1}.

Table 12.4 Some Typical Heats of Vaporization

Substance	$\Delta H_{\text{vaporization}}$ (kJ/mol)	Type of Attractive Force
H_2O	+43.9	Hydrogen bonding and London
NH_3	+21.7	Hydrogen bonding and London
HCl	+15.6	Dipole–dipole and London
SO_2	+24.3	Dipole–dipole and London
F_2	+5.9	London
Cl_2	+10.0	London
Br_2	+15.0	London
I_2	+22.0	London
CH_4	+8.16	London
C_2H_6	+15.1	London
C_3H_8	+16.9	London
C_6H_{14}	+30.1	London

Energy Changes and Intermolecular Attractions

When a liquid evaporates or a solid sublimes, the particles go from a situation in which the attractive forces are very strong to one in which the attractive forces are so small they can almost be ignored. Therefore, the values of $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$ give us directly the energy needed to separate molecules from each other. We can examine such values to obtain reliable comparisons of the strengths of intermolecular attractions.

In Table 12.4, notice that the heats of vaporization of water and ammonia are very large, which is just what we would expect for hydrogen-bonded substances. By comparison, CH_4, a nonpolar substance composed of atoms of a size similar to those of H_2O and NH_3, has a very small heat of vaporization. Note also that polar substances such as HCl and SO_2 have fairly large heats of vaporization compared with nonpolar substances. For example, compare HCl with Cl_2. Even though Cl_2 contains two relatively large atoms and therefore would be expected to have larger London forces than HCl, HCl has the larger $\Delta H_{\text{vaporization}}$. This must be due to dipole–dipole attractions between polar HCl molecules—attractions that are absent in nonpolar Cl_2.

■ The stronger the attractions, the more the potential energy will increase when the molecules become separated, and the larger will be the value of ΔH.

Heats of vaporization also reflect the factors that control the strengths of London forces. For example, the data in Table 12.4 show the effect of chain length on the intermolecular attractions between hydrocarbons; as the chain length increases from one carbon in CH_4 to six carbons in C_6H_{14}, the heat of vaporization also increases, showing that the London forces also increase. Similarly, the heats of vaporization of the halogens in Table 12.4 show that the strengths of London forces increase as the electron clouds of the particles become larger.

12.8 | Determining Heats of Vaporization

The way the vapor pressure varies with temperature, which was described in Section 12.5 and Figure 12.23, depends on the *heat of vaporization* of a substance. The relationship between vapor pressure and temperature, however, is not a simple proportionality. Instead, it involves *natural logarithms*, which are logarithms to the base *e*, as compared to the more familiar base-10 logarithms. (If you are unfamiliar with natural logarithms, please refer to Appendix A.)

The Clausius–Clapeyron Equation

Rudolf Clausius (1822–1888), a German physicist, and Benoit Clapeyron (1799–1864), a French engineer, used the principles of thermodynamics (a subject that's discussed in Chapter 19) to derive the following equation that relates the vapor pressure, heat of vaporization (ΔH_{vap}), and temperature:

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C \tag{12.2}$$

The quantity $\ln P$ is the natural logarithm of the vapor pressure, R is the gas constant expressed in energy units ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature, and C is a constant. Scientists call this the **Clausius–Clapeyron equation**.

The Clausius–Clapeyron equation provides a convenient graphical method for determining heats of vaporization from experimentally measured vapor pressure–temperature data. To see this, let's rewrite the equation as follows:

$$\ln P = \left(\frac{-\Delta H_{\text{vap}}}{R}\right)\frac{1}{T} + C$$

Recall from algebra that a straight line is represented by the general equation

$$y = mx + b$$

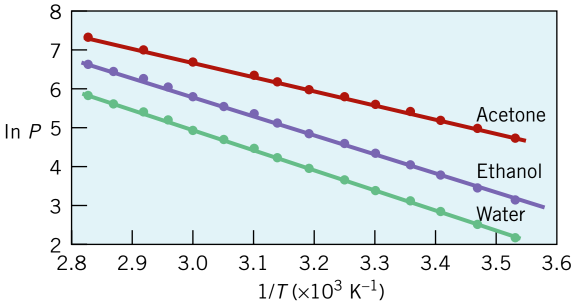
where x and y are variables, m is the slope, and b is the intercept of the line with the y axis. In this case, we can make the substitutions

$$y = \ln P \qquad x = \frac{1}{T} \qquad m = \left(\frac{-\Delta H_{\text{vap}}}{R}\right) \qquad b = C$$

Therefore, we have

$$\begin{array}{ccccc} \ln P & = & \left(\dfrac{-\Delta H_{\text{vap}}}{R}\right) & \dfrac{1}{T} & + \; C \\ \Updownarrow & & \Updownarrow & \Updownarrow & \Updownarrow \\ y & = & m & x & + \; b \end{array}$$

Thus, a graph of ln P versus $1/T$ should give a straight line that has a slope equal to $-\Delta H_{\text{vap}}/R$. Such straight-line relationships are illustrated in Figure 12.28, in which experimental data are plotted for water, acetone, and ethanol. From the graphs in Figure 12.28, the calculated values of ΔH_{vap} are as follows: for water, 43.9 kJ mol^{-1}; for acetone, 32.0 kJ mol^{-1}; and for ethanol, 40.5 kJ mol^{-1}.



The numbers along the horizontal axis are equal to $1/T$ values multiplied by 1000 to make the axis easier to label.

Figure 12.28 | **Plotting the Clausius–Clapeyron equation.** A graph showing plots of ln P versus $1/T$ for acetone, ethanol, and water.

Using Equation 12.2, a "two-point" form of the Clausius–Clapeyron equation can be derived that can be used to calculate ΔH_{vap} if the vapor pressure is known at two different temperatures. This equation is

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \textbf{(12.3)}$$

Clausius–Clapeyron equation

If we know the value of the heat of vaporization, Equation 12.3 can also be used to calculate the vapor pressure at some particular temperature (say, P_2 at a temperature T_2) if we already know the vapor pressure P_1 at a temperature T_1.

Example 12.3

Calculating the Heat of Vaporization from Temperatures and Vapor Pressures

Methanol, CH_3OH, experiences hydrogen bonding, dipole–dipole interactions, and London forces. At 64.6 °C, it has a vapor pressure of 1.00 atm, and at 12.0 °C, it has a vapor pressure of 0.0992 atm. What is the heat of vaporization for methanol?

■ **Analysis:** We are given two temperatures and two vapor pressures and we are asked to find the heat of vaporization. We will need to use the Clausius–Clapeyron equation to solve this problem.

■ **Assembling the Tools:** The main tool that we will use will be the application of the Clausius–Clapeyron equation, Equation 12.3, to find the heat of vaporization.

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solution: We are given the following data:

$$P_1 = 1.00 \text{ atm} \qquad t_1 = 64.6\ ^\circ\text{C}$$
$$P_2 = 0.0992 \text{ atm} \qquad t_2 = 12.0\ ^\circ\text{C}$$

In order to solve the equation we will have to convert the temperatures in °C into kelvins, K.

$$T_1 = 64.6\ ^\circ\text{C} + 273.15 = 337.8 \text{ K}$$
$$T_2 = 12.0\ ^\circ\text{C} + 273.15 = 285.2 \text{ K}$$

We do not have to convert the pressure units because they are in a ratio and the units will cancel out.

We will use 8.314 J mol^{-1} K^{-1} for the value for R—namely, the gas constant in units of energy.

Now we will work with the Clausius–Clayperon equation itself.

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

We need to solve for ΔH_{vap}, so let us rearrange the equation. If we multiply both sides of the equation by R and divide by $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, we will have ΔH_{vap} on one side of the equals sign and the rest on the other:

$$\Delta H_{\text{vap}} = \frac{\ln\dfrac{P_1}{P_2} \times R}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)}$$

Substituting the values for P_1, P_2, T_1, T_2, and R, we get

$$\Delta H_{\text{vap}} = \frac{\ln\dfrac{1.00 \text{ atm}}{0.0992 \text{ atm}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{\left(\dfrac{1}{285.2 \text{ K}} - \dfrac{1}{337.8 \text{ K}}\right)}$$

$$\Delta H_{\text{vap}} = \frac{2.311 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{0.003506 \text{ K}^{-1} - 0.00296 \text{ K}^{-1}}$$

$$\Delta H_{\text{vap}} = \frac{19.21 \text{ J mol}^{-1}\ \cancel{\text{K}^{-1}}}{0.000546\ \cancel{\text{K}^{-1}}}$$

$$\Delta H_{\text{vap}} = 35{,}180 \text{ J mol}^{-1} = 35.2 \text{ kJ mol}^{-1}$$

Is the Answer Reasonable? This problem involves a fair amount of the manipulation of equations. We need to check that we used the correct pressure with the correct temperature and that we placed them in the correct spot in the equation. Then, we need to review the math, and make sure that we did not make any math errors.

Practice Exercises

12.10 | At 0.00 °C, hexane, C_6H_{14}, has a vapor pressure of 45.37 mm Hg. Its ΔH_{vap} is 30.1 kJ mol^{-1}. What is the vapor pressure of hexane at 62.2 °C?

12.11 | Ethanol, with $\Delta H_{\text{vap}} = 40.5$ kJ mol^{-1}, has a higher ΔH_{vap} than methanol, which was calculated in Example 12.3 as 35.2 kJ mol^{-1}, due to its larger size and greater intermolecular forces. Because the ΔH_{vap} for ethanol is larger, we would expect that for the two liquids to reach the same vapor pressure, the temperature for ethanol would have to be higher. If the vapor pressure is 0.0992 atm at 27.3 °C, what would the temperature be when the vapor pressure is 1.00 atm?

12.9 | Le Châtelier's Principle and State Changes

Throughout this chapter, we have studied various dynamic equilibria. One example was the equilibrium that exists between a liquid and its vapor in a closed container. You learned that when the temperature of the liquid is increased in this system, its vapor pressure also increases. Let's briefly review why this occurs.

Initially, the liquid is in equilibrium with its vapor, which exerts a certain pressure. When the temperature is increased, equilibrium no longer exists because evaporation occurs more rapidly than condensation. Eventually, as the concentration of molecules in the vapor increases, *the system reaches a new equilibrium* in which there is more vapor and a little less liquid. The greater concentration of molecules in the vapor causes a larger pressure.

The way a liquid's equilibrium vapor pressure responds to a temperature change is an example of a general phenomenon. *Whenever a dynamic equilibrium is upset by some disturbance, the system changes in a way that will, if possible, bring the system back to equilibrium again.* It's also important to understand that in the process of regaining equilibrium, the system undergoes a net change. Thus, when the temperature of a liquid is raised, there is some net conversion of liquid into vapor as the system returns to equilibrium. When the new equilibrium is reached, the amounts of liquid and vapor are not the same as they were before.

Throughout the remainder of this book, we will deal with many kinds of equilibria, both chemical and physical. It would be very time consuming and sometimes very difficult to carry out a detailed analysis each time we wish to know the effects of some disturbance on an equilibrium system. Fortunately, there is a relatively simple and fast method for predicting the effect of a disturbance, one based on a principle proposed in 1888 by a brilliant French chemist, Henry Le Châtelier (1850–1936).

> **Le Châtelier's Principle**
> When a dynamic equilibrium in a system is upset by a disturbance, the system responds in a *direction* that tends to counteract the disturbance and, if possible, restore equilibrium.

TOOLS
Le Châtelier's principle

Let's see how we can apply Le Châtelier's principle to a liquid–vapor equilibrium that is subjected to a temperature increase. We cannot increase a temperature, of course, without adding heat. Thus, *the addition of heat is really the disturbing influence when a temperature is increased.* So, let's incorporate "heat" as a member of the equation used to represent the liquid–vapor equilibrium.

$$\text{heat} + \text{liquid} \rightleftharpoons \text{vapor} \tag{12.4}$$

Recall that we use double arrows, $\rightleftharpoons$, to indicate a dynamic equilibrium in an equation. They imply opposing changes happening at equal rates. Evaporation is endothermic, so the heat is placed on the left side of Equation 12.4 to show that heat is absorbed by the liquid when it changes to the vapor, and that heat is released when the vapor condenses to a liquid.

Le Châtelier's principle tells us that when we add heat to raise the temperature of the equilibrium system, the system will try to adjust in a way that absorbs some of the added heat. This can happen if some liquid evaporates, because vaporization is endothermic. When liquid evaporates, the amount of vapor increases and causes the pressure to rise. Thus, we have reached the correct conclusion in a very simple way—namely, that heating a liquid must increase its vapor pressure.

We often use the term **position of equilibrium** to refer to the relative amounts of the substances on opposite sides of the double arrows in an equilibrium expression such as Equation 12.4. Thus, we can think of how a disturbance affects the position of equilibrium. For example, increasing the temperature increases the amount of vapor and decreases the amount of liquid, and we say *the position of equilibrium has shifted*; in this case, it has shifted in the direction of the vapor, or it has *shifted to the right.* In using Le Châtelier's principle, it is often convenient to think of a disturbance as "shifting the position of equilibrium" in one direction or another in the equilibrium equation.

Practice Exercises

12.12 | Use Le Châtelier's principle to predict how a temperature increase will affect the vapor pressure of a solid. (*Hint:* Solid + heat $\rightleftharpoons$ vapor.)

12.13 | Designate whether each of the following physical processes is exothermic or endothermic: boiling, melting, condensing, subliming, and freezing. Can any of them be exothermic for some substances and endothermic for others?

12.10 | Phase Diagrams

Sometimes it is useful to know under what combinations of temperature and pressure a substance will be a liquid, a solid, or a gas, or the conditions of temperature and pressure that produce an equilibrium between any two phases. A simple way to determine this is to use a **phase diagram**—a graphical representation of the pressure–temperature relationships that apply to the equilibria between the phases of the substance.

TOOLS

Phase diagrams

Figure 12.29 is the phase diagram for water. On it, there are three lines that intersect at a common point. Equilibrium between phases exists everywhere along the lines. For example, line *BD* is the vapor pressure curve for liquid water. It gives the temperatures and pressures at which the liquid and vapor are able to coexist in equilibrium. Notice that when the temperature is 100 °C, the vapor pressure is 760 torr. Therefore, this diagram also tells us that water boils at 100 °C when the pressure is 1 atm (760 torr), because that is the temperature at which the vapor pressure equals 1 atm.

■ The melting point and boiling point can be read directly from the phase diagram.

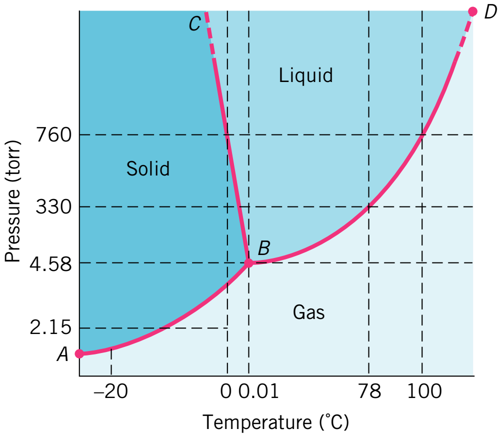


Figure 12.29 | **The phase diagram for water, distorted to emphasize certain features.** Temperatures and pressures corresponding to the dashed lines on the diagram are referred to in the text discussion.

The solid–vapor equilibrium line, *AB,* and the liquid–vapor line, *BD,* intersect at a common point, *B.* Because this point is on both lines, there is equilibrium between all three phases at the same time.

$$\begin{tikzcd} & \text{vapor} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \text{liquid} \arrow[ur, shift left] \arrow[rr, shift left] & & \text{solid} \arrow[ll, shift left] \arrow[ul, shift left] \end{tikzcd}$$

The temperature and pressure at which this triple equilibrium occurs define the **triple point** of the substance. For water, the triple point occurs at 0.01 °C and 4.58 torr. Every known chemical substance except helium has its own characteristic triple point, which is controlled by the balance of intermolecular forces in the solid, liquid, and vapor.

Line *BC,* which extends upward from the triple point, is the solid–liquid equilibrium line or *melting point line.* It gives temperatures and pressures at which the solid and the liquid are in equilibrium. At the triple point, the melting of ice occurs at +0.01 °C (and 4.58 torr); at 760 torr, melting occurs very slightly lower, at 0 °C. Thus, we can tell that *increasing the pressure on ice lowers its melting point.*

■ In the SI, the triple point of water is used to define the Kelvin temperature of 273.16 K.

The effect of pressure on the melting point of ice can be predicted using Le Châtelier's principle and the knowledge that a given mass of liquid water occupies *less volume* than the same mass of ice (i.e., liquid water is more dense than ice). Consider an equilibrium that is established between ice and liquid water at 0 °C and 1 atm in an apparatus like that shown in Figure 12.30.

$$\mathrm{H_2O}(s) \rightleftharpoons \mathrm{H_2O}(l)$$

If the piston is forced in slightly, the pressure increases. According to Le Châtelier's principle, the system should respond, if possible, in a way that reduces the pressure. This can happen if some of the ice melts, so the ice–liquid mixture won't require as much space.

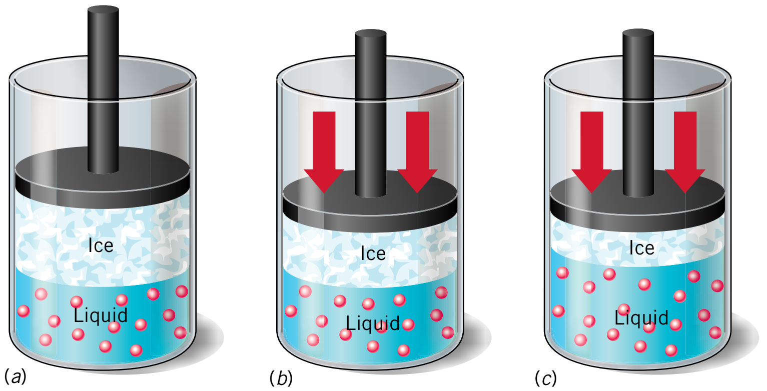


Figure 12.30 | **The effect of pressure on the equilibrium, $H_2O(solid) \rightleftharpoons H_2O(liquid)$.** (*a*) The system is at equilibrium between water as a liquid and water as a solid. (*b*) Pushing down on the piston decreases the volume of both the ice and liquid water by a small amount and increases the pressure. (*c*) Some of the ice melts, producing the more dense liquid. As the total volume of ice and liquid water decreases, the pressure drops and equilibrium is restored.

Then the molecules won't push as hard against each other and the walls, and the pressure will drop. Thus, a pressure-increasing disturbance to the system favors a volume-decreasing change, which corresponds to the melting of some ice.

Now suppose we have ice at a pressure just below the solid–liquid line, *BC.* If, *at constant temperature,* we raise the pressure to a point just above the line, the ice will melt and become a liquid. This could only happen if the melting point decreases as the pressure increases.

Water is very unusual. Almost all other substances have melting points that increase with increasing pressure, as illustrated by the phase diagram for carbon dioxide (Figure 12.31). For CO_2 the solid–liquid line slants to the right (it slanted to the left for water). Also notice that carbon dioxide has a triple point that's above 1 atm. At atmospheric pressure, the only equilibrium that can be established is between solid carbon dioxide and its vapor. At a pressure of 1 atm, this equilibrium occurs at a temperature of −78 °C. This is the temperature of dry ice, which sublimes at atmospheric pressure at −78 °C.

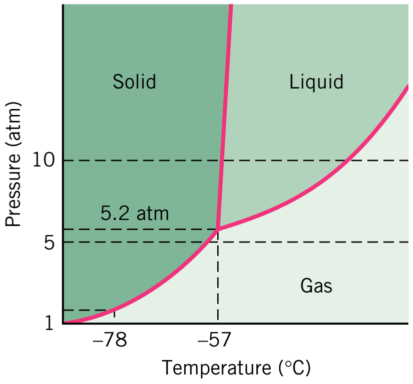


Figure 12.31 | **The phase diagram for carbon dioxide.**

Interpreting a Phase Diagram

Besides specifying phase equilibria, the three intersecting lines on a phase diagram serve to define regions of temperature and pressure at which only a single phase can exist. For example, between lines *BC* and *BD* in Figure 12.29 are temperatures and pressures at which water exists as a liquid without being in equilibrium with either vapor or ice. At 760 torr, water is a liquid anywhere between 0 °C and 100 °C. According to the diagram, we can't have ice with a temperature of 25 °C if the pressure is 760 torr (which, of course, you already knew; ice never has a temperature of 25 °C.) The diagram also says that we can't have water vapor with a pressure of 760 torr when the temperature is 25 °C (which, again, you already knew; the temperature has to be taken to 100 °C for the vapor pressure to reach 760 torr). Instead, the phase diagram indicates that the *only* phase for pure water at 25 °C and 1 atm is the liquid. Below 0 °C at 760 torr, water is a solid; above 100 °C at 760 torr, water is a vapor. On the phase diagram for water, the phases that can exist in the different temperature–pressure regions are marked.

Example 12.4
Interpreting a Phase Diagram

What phase would we expect for water at 0 °C and 4.58 torr?

- **Analysis:** The words "What phase . . ." as well as the specified temperature and pressure, suggest that we refer to the phase diagram of water (Figure 12.29).
- **Assembling the Tools:** The tool we will use is the phase diagram of water.

■ **Solution:** First, we find 0 °C on the temperature axis of the phase diagram of water. Then, we move upward until we intersect a line corresponding to 4.58 torr. This intersection occurs in the "solid" region of the diagram. At 0 °C and 4.58 torr, then, water exists as a solid.

■ **Is the Answer Reasonable?** We've seen that the freezing point of water increases slightly when we lower the pressure, so below 1 atm, water should still be a solid at 0 °C. That agrees with the answer we obtained from the phase diagram.

Example 12.5
Interpreting a Phase Diagram

What phase changes occur if water at 0 °C is gradually compressed from a pressure of 2.15 torr to 800 torr?

■ **Analysis:** Asking "what phase changes occur" suggests once again that we use the phase diagram of water (Figure 12.29).

■ **Assembling the Tools:** Just as in Example 12.4, the tool we will use is the phase diagram of water.

■ **Solution:** According to the phase diagram, at 0 °C and 2.15 torr, water exists as a gas (water vapor). As the vapor is compressed, we move upward along the 0 °C line until we encounter the solid–vapor line. There, an equilibrium will exist as compression gradually transforms the gas into solid ice. Once all of the vapor has frozen, further compression raises the pressure and we continue the climb along the 0 °C line until we next encounter the solid–liquid line at 760 torr. As further compression takes place, the solid will melt. After all of the ice has melted, the pressure will continue to climb while the water remains a liquid. At 800 torr and 0 °C, the water will be liquid. The phase changes are gas to solid to liquid.

■ **Is the Answer Reasonable?** There's not too much we can do to check all this except to take a fresh look at the phase diagram. We do expect that above 760 torr, the melting point of ice will be less than 0 °C, so at 0 °C and 800 torr we can anticipate that water will be a liquid.

Practice Exercises

12.14 | The equilibrium line from point *B* to *D* in Figure 12.29 is present in another figure in this chapter. Identify what that line represents. (*Hint:* A review of the other figures will reveal the nature of the line.)

12.15 | What phase changes will occur if water at −20 °C and 2.15 torr is heated to 50 °C under constant pressure?

12.16 | What phase will water be in if it is at a pressure of 330 torr and a temperature of 50 °C?

Supercritical Fluids

For water (Figure 12.29), the vapor pressure line for the liquid, which begins at point *B*, terminates at point *D*, which is known as the **critical point**. The temperature and pressure at *D* are called the **critical temperature, T_c**, and the **critical pressure, P_c**. Above the critical temperature, a distinct liquid phase cannot exist, *regardless of the pressure.*

Figure 12.32 illustrates what happens to a substance as it approaches its critical point. In Figure 12.32*a*, we see a liquid in a container with some vapor above it. We can distinguish between the two phases because they have different densities, which causes them to bend light differently. This allows us to see the interface, or surface, between the more

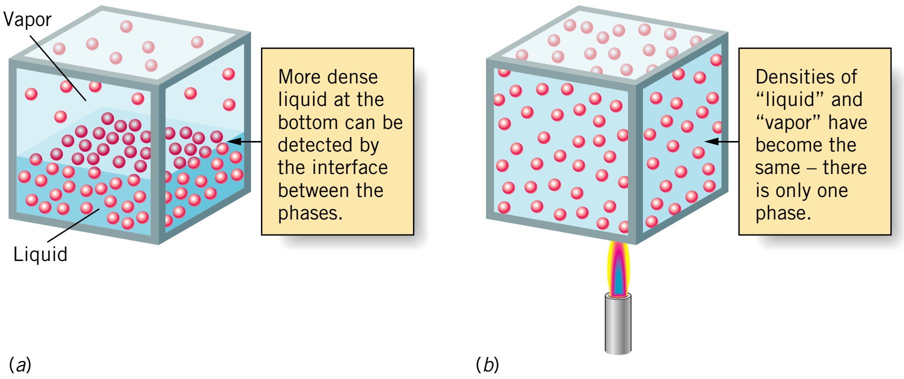

Vapor
Liquid
More dense liquid at the bottom can be detected by the interface between the phases.
(a)
Densities of "liquid" and "vapor" have become the same – there is only one phase.
(b)

Figure 12.32 | **Changes that are observed when a liquid is heated in a sealed container.** (*a*) Below the critical temperature. (*b*) Above the critical temperature.

dense liquid and the less dense vapor. If this liquid is now heated, two things happen. First, more liquid evaporates. This causes an increase in the number of molecules per cubic centimeter of vapor, which, in turn, causes the density of the vapor to increase. Second, the liquid expands. This means that a given mass of liquid occupies more volume, so its density decreases. As the temperature of the liquid and vapor continue to increase, the vapor density rises and the liquid density falls; they approach each other. Eventually the densities become equal, and a separate liquid phase no longer exists; everything is the same (see Figure 12.32*b*). The highest temperature at which a liquid phase still exists is the critical temperature, and the pressure of the vapor at this temperature is the critical pressure. A substance that has a temperature above its critical temperature and a density near its liquid density is described as a **supercritical fluid**. Supercritical fluids have some unique properties that make them excellent solvents, and one that is particularly useful is supercritical carbon dioxide, which is used as a solvent to decaffeinate coffee.

CHEMISTRY OUTSIDE THE CLASSROOM | 12.1

Decaffeinated Coffee and Supercritical Carbon Dioxide

Many people prefer to avoid caffeine, yet still enjoy their cup of coffee. For them, decaffeinated coffee is just the thing. To satisfy this demand, coffee producers remove caffeine from the coffee beans before roasting them. Several methods have been used, some of which use solvents such as methylene chloride (CH_2Cl_2) or ethyl acetate ($CH_3CO_2C_2H_5$) to dissolve the caffeine. Even though only trace amounts of these solvents remain after the coffee beans are dried, there are those who would prefer not to have any such chemicals in their coffee. And that's where carbon dioxide comes into the picture.

Decaffeinated Coffee
M. ROHRS'

(Andy Washnik)

It turns out that supercritical carbon dioxide is an excellent solvent for many organic substances, including caffeine. To make supercritical carbon dioxide, gaseous CO_2 is heated to a temperature (typically ~80 °C) above its critical temperature of 31 °C. It is then compressed to about 200 atm. This gives it a density near that of a liquid, but with some properties of a gas. The fluid has a very low viscosity and readily penetrates coffee beans that have been softened with steam, drawing out the water and the caffeine. After several hours, the CO_2 has removed as much as 97% of the caffeine, and the fluid containing the water and caffeine is then drawn off. When the pressure of the supercritical CO_2 solution is reduced, the CO_2 turns to a gas and the water and caffeine separate. The caffeine is recovered and sold to beverage or pharmaceutical companies. Meanwhile, the pressure over the coffee beans is also reduced and the beans are warmed to about 120 °C, causing residual CO_2 to evaporate. Because CO_2 is not a toxic gas, any traces of CO_2 that remain are harmless.

Decaffeination of coffee is not the only use of supercritical CO_2. It is also used to extract the essential flavor ingredients in spices and herbs for use in a variety of products. As with coffee, using supercritical CO_2 as a solvent completely avoids any potential harm that might be caused by small residual amounts of other solvents.

Table 12.5 Some Critical Temperatures and Pressures

Compound	T_c (°C)	P_c (atm)
Water	374.1	217.7
Ammonia	132.5	112.5
Carbon dioxide	31	72.9
Ethane (C_2H_6)	32.2	48.2
Methane (CH_4)	−82.1	45.8
Helium	−267.8	2.3

The values of the critical temperature and critical pressure are unique for every chemical substance and are controlled by the intermolecular attractions (see Table 12.5). Notice that liquids with strong intermolecular attractions, like water, tend to have high critical temperatures. Under pressure, the strong attractions between the molecules are able to hold them together in a liquid state even when the molecules are jiggling about violently at an elevated temperature. In contrast, substances with weak intermolecular attractions, such as methane and helium, have low critical temperatures. For these substances, even the small amounts of kinetic energy possessed by the molecules at low temperatures is sufficient to overcome the intermolecular attractions and prevent the molecules from sticking together as a liquid, despite being held close together under high pressure.

Liquefaction of Gases

When a gaseous substance has a temperature below its critical temperature, it is capable of being liquefied by compressing it. For example, carbon dioxide is a gas at room temperature (approximately 25 °C). This is below its critical temperature of 31 °C. If the $CO_2(g)$ is gradually compressed, a pressure will eventually be reached that lies on the liquid–vapor curve for CO_2, and further compression will cause the CO_2 to liquefy. In fact, that's what happens when a CO_2 fire extinguisher is filled; the CO_2 that's pumped in is a liquid under high pressure. If you shake a filled CO_2 fire extinguisher, you can feel the liquid sloshing around inside, provided the temperature of the fire extinguisher is below 31 °C (88 °F). When the fire extinguisher is used, a valve releases the pressurized CO_2, which rushes out to extinguish the fire.

Gases such as O_2 and N_2, which have critical temperatures far below 0 °C, can never be liquids at room temperature. When they are compressed, they simply become high-pressure gases. To make liquid N_2 or O_2, the gases must be made very cold as well as be compressed to high pressures.

■ On a very hot day, when the temperature is in the 90s, a filled CO_2 fire extinguisher won't give the sensation that it's filled with a liquid. At such temperatures, the CO_2 is in a supercritical state and no separate liquid phase exists.

■ A high degree of regularity is the principal feature that makes solids different from liquids. A liquid lacks this long-range repetition of structure because the particles in a liquid are jumbled and disorganized as they move about.

12.11 | Structures of Crystalline Solids

When many substances freeze, or when they separate as a solid from a solution, they tend to form crystals that have highly regular features. For example, Figure 12.33 is a photograph of crystals of sodium chloride—ordinary table salt. Notice that each particle is very nearly a perfect little cube. Whenever a solution of NaCl is evaporated, the crystals that form have edges that intersect at 90° angles. Thus, cubes are the norm for NaCl.

Crystals in general tend to have flat surfaces that meet at angles that are characteristic of the substance. The regularity of these surface features reflects the high degree of order among the particles that lie within the crystal. This is true whether the particles are atoms, molecules, or ions.

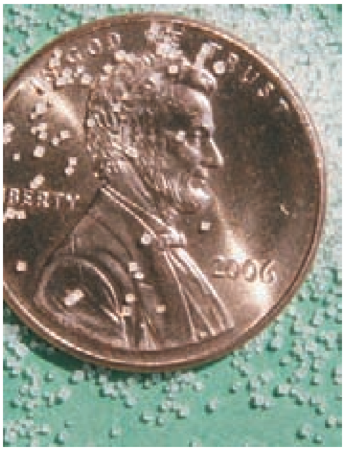


Figure 12.33 | **Crystals of table salt.** The size of the tiny cubic sodium chloride crystals can be seen in comparison with a penny. *(The Photo Works)*

Lattices and Unit Cells

Any repetitive pattern has a symmetrical aspect about it, whether it is a wallpaper design or the orderly packing of particles in a crystal (Figure 12.34). For example, we can recognize certain repeating distances between the elements of the pattern, and we can see that the lines along which the elements of the pattern repeat are at certain angles to each other.

To concentrate on the symmetrical features of a repeating structure, it is convenient to describe it in terms of a set of points that have the same repeat distances as the structure, arranged along lines oriented at the same angles. Such a pattern of points is called a **lattice**,

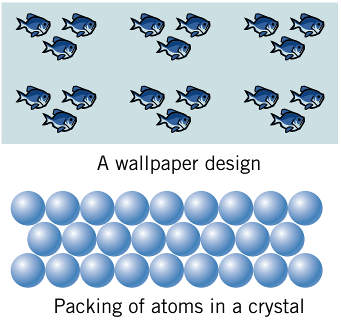

A wallpaper design
Packing of atoms in a crystal

Figure 12.34 | **Symmetry among repetitive patterns.** A wallpaper design and particles arranged in a crystal each show a repeating pattern of structural units. The pattern can be described by the distances between the repeating units and the angles along which the repetition of structure occurs.

and when we apply it to describe the packing of particles in a solid, we often call it a **crystal lattice.**

In a crystal, the number of particles is enormous. If you could imagine being at the center of even the tiniest crystal, you would find that the particles go on as far as you can see in every direction. Describing the positions of all these particles or their lattice points is impossible and, fortunately, unnecessary. All we need to do is describe the repeating unit of the lattice, which we call the *unit cell.* To see this, and to gain an insight into the usefulness of the lattice concept, let's begin in two dimensions.

In Figure 12.35, we see a two-dimensional *square lattice*, which means the lattice points lie at the corners of squares. The repeating unit of the lattice, its **unit cell**, is indicated in the drawing. If we began with this unit cell, we could produce the entire lattice by moving it repeatedly left and right and up and down by distances equal to its edge length. In this sense, all of the properties of a lattice are contained in the properties of its unit cell.

An important fact about lattices is that the same lattice can be used to describe many different designs or structures. For example, in Figure 12.35*b*, we see a design formed by associating a pink heart with each lattice point. Using a square lattice, we could form any number of designs just by using different design elements (for example, a rose or a diamond) or by changing the lengths of the edges of the unit cell. *The only requirement is that the same design element must be associated with each lattice point.* In other words, if there is a rose at one lattice point, then there must be a rose at all the other lattice points.

Extending the lattice concept to three dimensions is relatively straightforward. Illustrated in Figure 12.36 is a **simple cubic** (also called a **primitive cubic**) lattice, the simplest and most symmetrical three-dimensional lattice. Its unit cell, the **simple cubic unit cell**, is a cube with lattice points only at its eight corners. Figure 12.36*c* shows the packing of atoms in a substance that might crystallize in a simple cubic lattice, as well as the unit cell for that substance.[3]

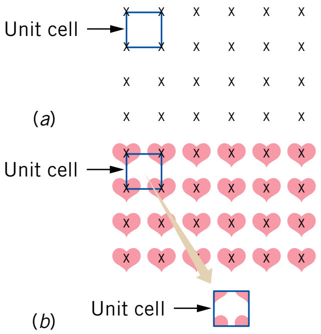


Figure 12.35 | **A two-dimensional lattice.** (*a*) A simple square lattice, for which the unit cell is a square with lattice points at the corners. (*b*) A wallpaper pattern formed by associating a design element (pink heart) with each lattice point. The x centered on each heart corresponds to a lattice point. The unit cell contains portions of a heart at each corner.

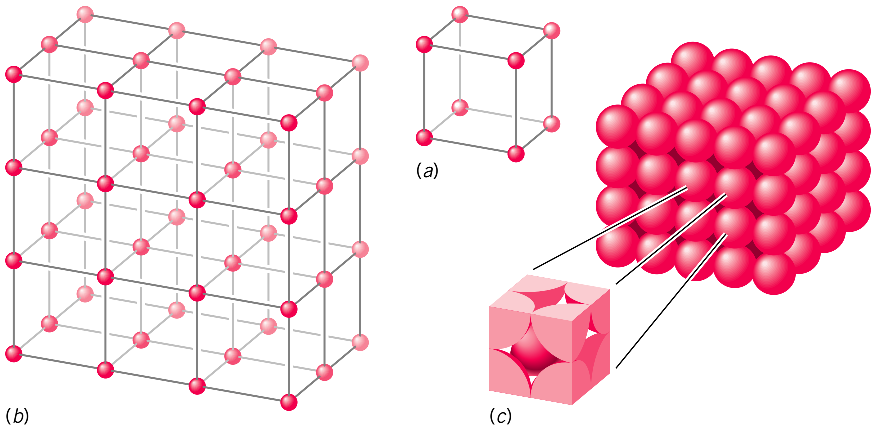


Figure 12.36 | **A three-dimensional simple cubic lattice.** (*a*) A simple cubic unit cell showing the locations of the lattice points. (*b*) A portion of a simple cubic lattice built by stacking simple cubic unit cells. (*c*) A hypothetical substance that forms crystals having a simple cubic lattice with identical atoms at the lattice points. Only a portion of each atom lies within this particular unit cell.

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[3] Polonium is the only metal that has an allotrope that crystallizes in a simple cubic lattice. Some compounds, however, do form simple cubic lattices.

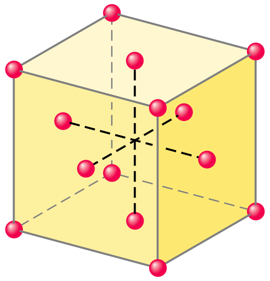


Figure 12.37 | **A face-centered cubic unit cell.** Lattice points are found at each of the eight corners and in the center of each face.

As with the two-dimensional lattice, we could use the same simple cubic lattice to describe the structures of many different substances. The *sizes* of the unit cells would vary because the sizes of atoms vary, but the essential symmetry of the stacking would be the same in them all. This fact about lattices makes it possible to describe limitless numbers of different compounds with just a limited set of three-dimensional lattices. In fact, it has been shown mathematically that there are only 14 different three-dimensional lattices possible, which means that all of the chemical substances that can exist must form crystals with one or another of these 14 lattice types.

The 14 lattice types are shown in Table 12.6. There are seven basic lattice shapes, which depend on the lengths of the sides, a_1, a_2, and a_3, and the angles between the edges of the shapes, α_{12}, α_{23}, and α_{13}. The variations on the basic shapes give the lattice types. The simple shape only has lattice points in the corners of the lattice. The body-centered structures have lattice points in the middle of the cells. The base-centered structures have a lattice point on two opposing faces, and the face-centered structures have lattice points on all of the faces.

Cubic Lattices

Cubic unit cells

Cubic lattices are the simplest lattices because all of the sides have the same length and all of the angles are 90°. In addition to simple cubic, two other cubic lattices are possible: face-centered cubic and body-centered cubic. The **face-centered cubic** (abbreviated **fcc**) **unit cell** has lattice points (and, therefore, identical particles) at each of its eight corners plus another in the center of each face, as shown in Figure 12.37. Many common metals—copper, silver, gold, aluminum, and lead, for example—form crystals that have face-centered cubic lattices. Each of these metals has the same *kind* of lattice, but the *sizes* of their unit cells differ because the sizes of the atoms differ (see Figure 12.38).

The **body-centered cubic (bcc) unit cell** has lattice points at each corner plus one in the center of the cell, as illustrated in Figure 12.39. The body-centered cubic lattice is also common among a number of metals; examples include chromium, iron, and platinum. Again, these are substances with the same *kind* of lattice, but the dimensions of the lattices vary because of the *different sizes* of the particular atoms.

Not all unit cells are cubic. Some have edges of different lengths or edges that intersect at angles other than 90°, as shown in Table 12.6. Although you should be aware of the existence of other unit cells and lattices, we will limit the remainder of our discussion to cubic lattices and their unit cells.

Counting atoms in unit cells

If we look at the unit cell of the face-centered cubic structure of copper in Figure 12.38, we can see that the atoms are cut up into parts. We can show that the parts add up to whole atoms. Notice that when the unit cell is "carved out" of the crystal, we find only part

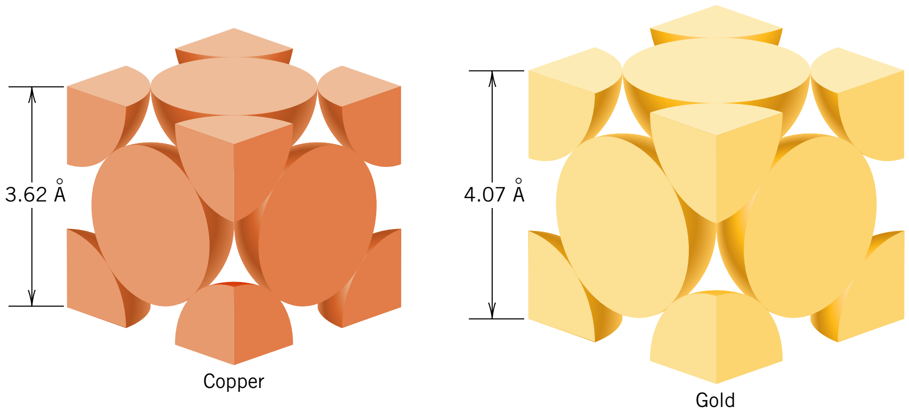


Figure 12.38 | **Unit cells for copper and gold.** These metals both crystallize in a face-centered cubic structure with similar face-centered cubic unit cells. The atoms are arranged in the same way, but their unit cells have edges of different lengths because the atoms are of different sizes. (1 Å = 1×10^{-10} m)

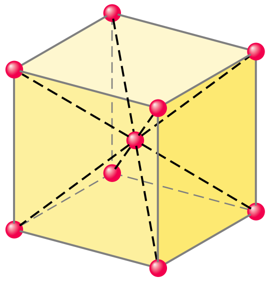
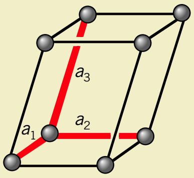
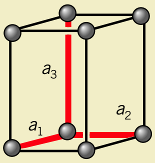
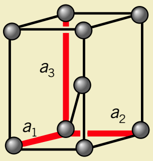
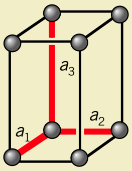
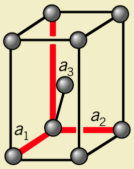
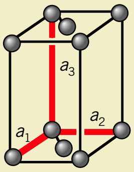
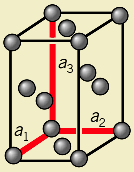
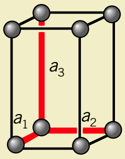
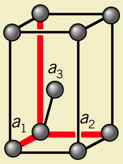
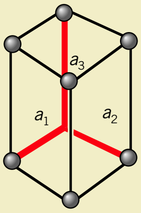
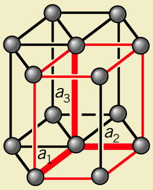
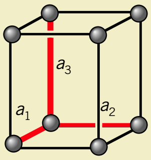
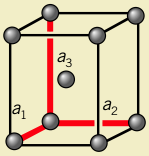
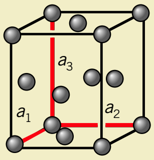
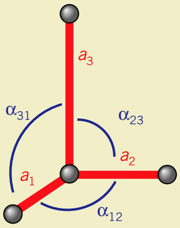


Figure 12.39 | **A body-centered cubic unit cell.** Lattice points are located at each of the eight corners and in the center of the unit cell.

Table 12.6 Crystal Lattice Types

The 7 Lattices		The 14 Lattice Types			
		Simple	Body-Centered	Base-Cenrered	Face-Centered
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31} \neq 90°$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120° \neq 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				


a_3
α_{31}
α_{23}
a_2
a_1
α_{12}

of an atom ($\frac{1}{8}$th of an atom, actually) at each corner. The rest of each atom resides in adjacent unit cells. Because the unit cell has eight corners, if we put all the corner pieces together we would obtain one complete atom.

$$8 \text{ corners} \times \frac{\frac{1}{8} \text{ atom}}{\text{corner}} = 1 \text{ atom}$$

Now, if we look at the atoms in the face, only half of each atom lies inside of the unit cell, but there are six faces and therefore six half atoms, for a total of three atoms.

$$6 \text{ corners} \times \frac{\frac{1}{2} \text{ atom}}{\text{corner}} = 3 \text{ atoms}$$

The total number of atoms in the unit cell is four atoms: three from the faces and one from the corners. In addition, if an atom is on the edge of a cube, then it contributes $\frac{1}{4}$ of an atom to the unit cell.

Compounds that Crystallize with Cubic Lattices

We have seen that a number of metals have cubic lattices. The same is true for many compounds. Figure 12.40, for example, is a view of a portion of a sodium chloride crystal. The Cl^- ions (green) are shown at the lattice points that correspond to a face-centered cubic unit cell. The smaller gray spheres represent Na^+ ions. Notice that they fill the spaces between the Cl^- ions. If we look at the locations of identical particles (e.g., Cl^-), we find them at lattice points that describe a face-centered cubic structure. Thus, sodium chloride is said to have a face-centered cubic lattice, and the cubic shape of this lattice is what accounts for the cubic shape of a sodium chloride crystal.

Many of the alkali halides (Group 1A–7A compounds), such as NaBr and KCl, crystallize with fcc lattices that have the same arrangement of ions as is found in NaCl. In fact, this arrangement of ions is so common that it's called the **rock salt structure** (rock salt is the mineral name of NaCl). Because sodium bromide and potassium chloride both have the same kind of lattice as sodium chloride, Figure 12.40 also could be used to describe their unit cells. The *sizes* of their unit cells are different, however, because K^+ is larger than Na^+ and Br^- is larger than Cl^-.

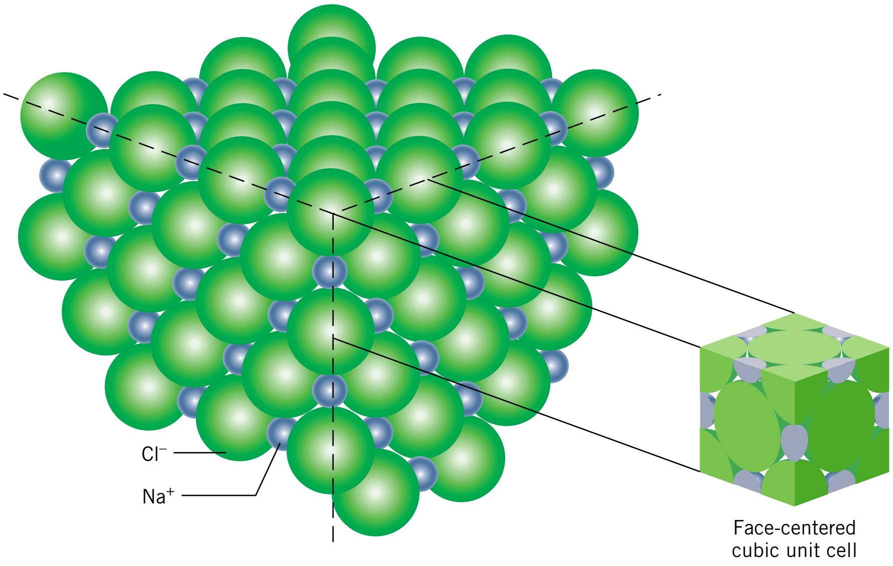


Figure 12.40 | **The packing of ions in a sodium chloride crystal.** Chloride ions are shown here to be associated with the lattice points of a face-centered cubic unit cell, with the sodium ions placed between the chloride ions.

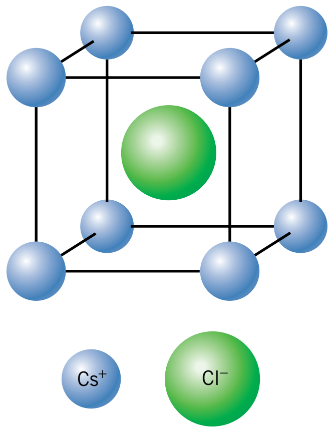


Figure 12.41 | **The unit cell for cesium chloride, CsCl.** The chloride ion is located in the center of the unit cell. The ions are not shown full-size to make it easier to see their locations in the unit cell.

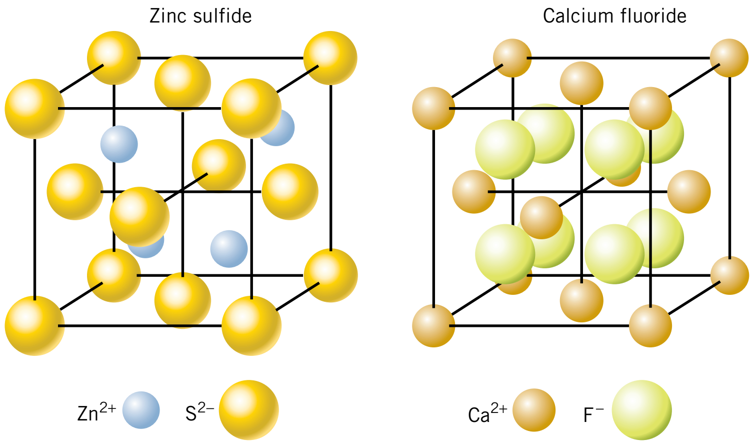


Figure 12.42 | **Crystal structures based on the face-centered cubic lattice.** Both zinc sulfide, ZnS, and calcium fluoride, CaF_2, have crystal structures that fit a face-centered cubic lattice. In ZnS, the sulfide ions are shown at the fcc lattice sites with the four zinc ions entirely within the unit cell. In CaF_2, the calcium ions are at the lattice points with the eight fluorides entirely within the unit cell. *Note:* The ions are not shown full-size to make it easier to see their locations in the unit cells.

Other examples of cubic unit cells are shown in Figures 12.41 and 12.42. The structure of cesium chloride in Figure 12.41 is simple cubic, although at first glance it may appear to be body-centered. This is because in a crystal lattice, identical chemical units must be at each lattice point. In CsCl, Cs^+ ions are found at the corners, but not in the center, so the Cs^+ ions describe a simple cubic unit cell.

Both zinc sulfide and calcium fluoride in Figure 12.42 have face-centered cubic unit cells that differ from that for sodium chloride, which illustrates once again how the same basic kind of lattice can be used to describe a variety of chemical structures.

Effects of Stoichiometry on Crystal Structure

At this point, you may wonder why a compound crystallizes with a particular structure. Although this is a complex issue, at least one factor is the stoichiometry of the substance. Because the crystal is made up of a huge number of identical unit cells, the stoichiometry within the unit cell must match the overall stoichiometry of the compound. Let's see how this applies to sodium chloride.

Example 12.6

Counting Atoms or Ions in a Unit Cell

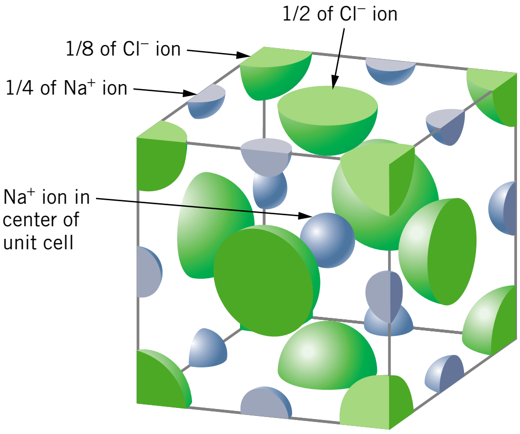
How many sodium and chloride ions are there in the unit cell of sodium chloride?

■ **Analysis:** To answer this question, we have to look closely at the unit cell of sodium chloride. The critical link is realizing that when the unit cell is carved out of the crystal, it encloses *parts of ions*, so we have to determine how many *whole* sodium and chloride ions can be constructed from the pieces within a given unit cell.

■ **Assembling the Tools:** We will use the tools of counting atoms in the unit cell of sodium chloride to see how many parts of atoms there are in the unit cell.

■ **Solution:** Let's look at the "exploded" view of the NaCl unit cell shown in Figure 12.43. We have parts of chloride ions at the corners and in the center of each face. Let's add the parts.

Figure 12.43 | **An exploded view of the unit cell of sodium chloride.**



For chloride:

$$8 \text{ corners} \times \frac{1}{8}\text{Cl}^- \text{ per corner} = 1 \text{ Cl}^-$$

$$6 \text{ faces} \times \frac{1}{2}\text{Cl}^- \text{ per face} = 3 \text{ Cl}^-$$

$$\text{Total} = 4 \text{ Cl}^-$$

For the sodium ions, we have parts along each of the 12 edges plus one whole Na^+ ion in the center of the unit cell. Let's add them.

For sodium:

$$12 \text{ edges} \times \frac{1}{4}\text{Na}^+ \text{ per edge} = 3 \text{ Na}^+$$

$$1 \text{ Na}^+ \text{ in the center} = 1 \text{ Na}^+$$

$$\text{Total} = 4 \text{ Na}^+$$

Thus, in one unit cell, there are four chloride ions and four sodium ions.

■ **Is the Answer Reasonable?** The ratio of the ions is 4 to 4, which is the same as 1 to 1. That's the ratio of the ions in NaCl, so the answer is reasonable.

Practice Exercises

12.17 | Chromium crystallizes in a body centered cubic structure. How many chromium atoms are in its unit cell? (*Hint:* Use Figure 12.39 as a guide.)

12.18 | What is the ratio of the ions in the unit cell of cesium chloride, which is shown in Figure 12.41? Does this match the formula of cesium chloride? Why is this important?

The calculation in Example 12.6 shows why NaCl can have the crystal structure it does; the unit cell has the proper ratio of cations to anions. It also shows why a compound such as $CaCl_2$ could *not* crystallize with the same kind of unit cell as NaCl. The sodium chloride structure demands a 1 to 1 ratio of cation to anion, so it could not be used by $CaCl_2$ (which has a 1 to 2 cation-to-anion ratio).

Closest-Packed Solids

For many solids, particularly metals, the type of crystal structure formed is controlled by maximizing the number of neighbors that surround a given atom. The more neighbors an atom has, the greater are the number of interatomic attractions and the greater is the

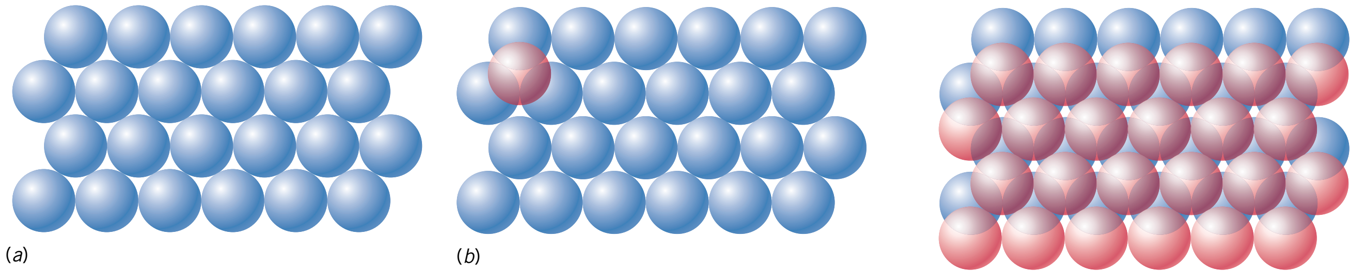


Figure 12.44 | **Packing of spheres.** (*a*) One layer of closely packed spheres. (*b*) A second layer is started by placing a sphere (colored red) in a depression formed between three spheres in the first layer. (*c*) A second layer of sphere shown slightly transparent so we can see how the atoms are stacked over the first layer.

energy lowering when the solid forms. Structures that achieve the maximum density of packing are known as **closest-packed structures**, and there are two of them that are only slightly different. To visualize how these are produced, let's look at ways to pack spheres of identical size.

Figure 12.44*a* illustrates a layer of blue spheres packed as tightly as possible. Notice that each sphere is surrounded by six others that it touches in this layer. When we add a second layer, each sphere (red) rests in a depression formed by three spheres in the first layer, as illustrated in Figures 12.44*b* and 12.44*c*.

The difference between the two closest-packed structures lies in the relative orientations of the spheres in the first layer and those that form the third layer. In Figure 12.45*a*, the green spheres in the third layer each lie in a depression between red spheres that is directly above a depression between blue spheres in the first layer—that is, none of these three layers is directly above each other. This kind of packing is called **cubic closest packing**, abbreviated **ccp**, because when viewed from a different perspective, the atoms are located at positions corresponding to a face-centered cubic lattice (Figure 12.46*a*). Figure 12.45*b* describes the other closest-packed structure in which a green sphere in the third layer rests in a depression between red spheres and directly above a blue sphere in the first

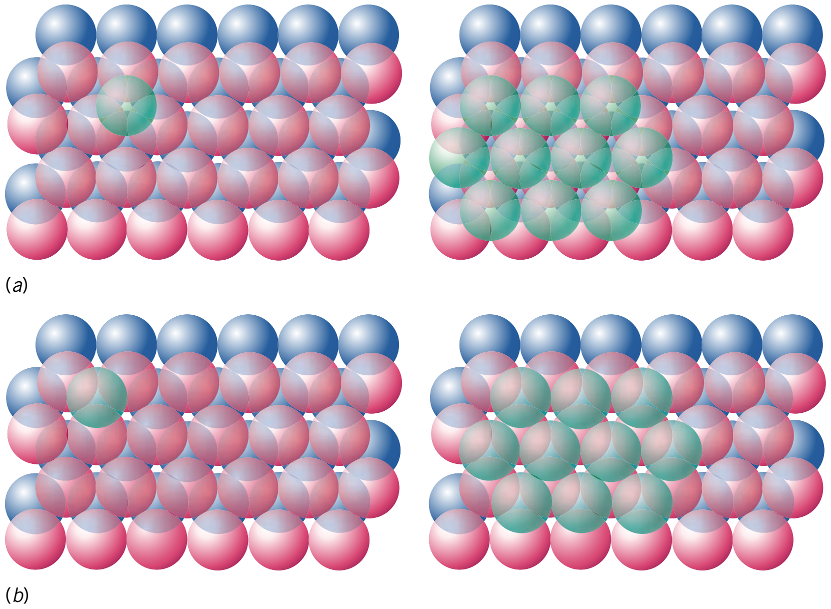


Figure 12.45 | **Closest-packed structures.** (*a*) Cubic closest packing of spheres. (*b*) Hexagonal closest packing of spheres. In both (*a*) and (*b*) the left diagram illustrates the position of one atom on the third layer and the right diagram shows the third layer partially complete. Notice that there are subtle differences between the two modes of packing.

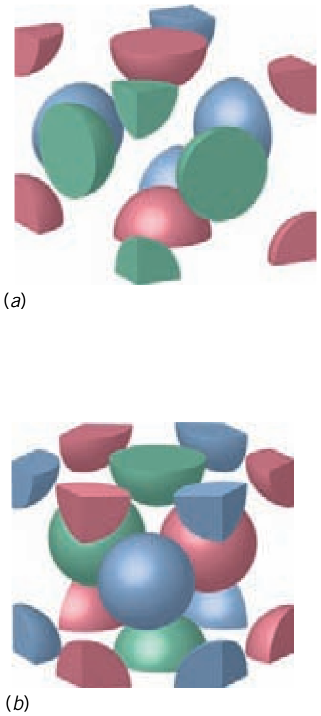
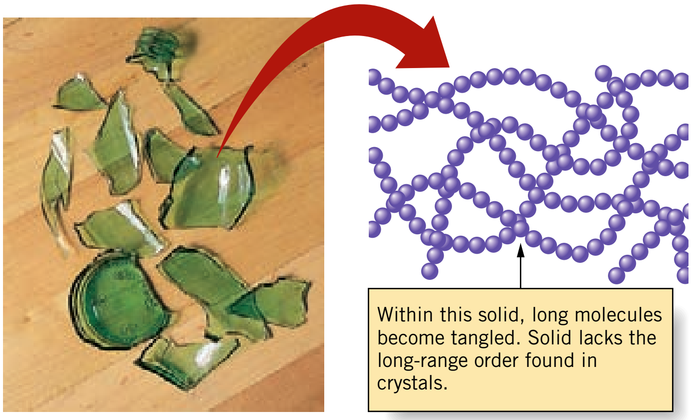


Figure 12.46 | **Unit cells of closest-packed structures.** (*a*) Cubic closest packing of spheres. (*b*) Hexagonal closest packing of spheres.

layer. This arrangement of spheres is called **hexagonal closest packing,** abbreviated **hcp** (Figure 12.46*b*). This corresponds to the hexagonal structure shown in Table 12.6.

In the hcp structure, the layers alternate in an A-B-A-B . . . pattern, where A stands for the orientations of the first, third, fifth, etc., layers, and B stands for the orientations of the second, fourth, sixth, etc., layers. Thus, the spheres in the third, fifth, seventh, etc., layers are directly above those in the first, while spheres in the fourth, sixth, eighth, etc., layers are directly above those in the second. In the ccp structure, there is an A-B-C-A-B-C. . . pattern. The first layer is oriented like the fourth, the second like the fifth, and the third like the sixth.



Within this solid, long molecules become tangled. Solid lacks the long-range order found in crystals.

Figure 12.47 | **Glass is a noncrystalline solid.** When glass breaks, the pieces have sharp edges, but their surfaces are not flat planes. This is because in an amorphous solid like glass, long molecules (much simplified here for clarity) are tangled and disorganized, so there is no long-range order characteristic of a crystal. *(Robert Capece)*

Both the ccp and hcp structures yield very efficient packing of identically sized atoms. In both structures, each atom is in contact with 12 neighboring atoms—six atoms in its own layer, three atoms in the layer below, and three atoms in the layer above. Metals that crystallize with the ccp structure include copper, silver, gold, aluminum, and lead. Metals with the hcp structure include titanium, zinc, cadmium, and magnesium.

Noncrystalline Solids

If a cubic salt crystal is broken, the pieces still have flat faces that intersect at 90° angles. If you shatter a piece of glass, on the other hand, the pieces often have surfaces that are not flat. Instead, they tend to be smooth and curved (see Figure 12.47). This behavior illustrates a major difference between crystalline solids, such as NaCl, and noncrystalline solids, also called **amorphous solids**, such as glass.

The word *amorphous* is derived from the Greek word *amorphos,* which means "without form." Amorphous solids do not have the kinds of long-range repetitive internal structures that are found in crystals. In some ways their structures, being jumbled, are more like liquids than solids. Examples of amorphous solids are ordinary glass and many plastics. In fact, the word **glass** is often used as a general term to refer to any amorphous solid.

As suggested in Figure 12.47, substances that form amorphous solids often consist of long, chain-like molecules that are intertwined in the liquid state somewhat like long strands of cooked spaghetti. To form a crystal from the melted material, these long molecules would have to become untangled and line up in specific patterns. However, as the liquid cools, the molecules slow down. Unless the liquid is cooled extremely slowly, the molecular motion decreases too rapidly for the untangling to take place, and the substance solidifies with the molecules still intertwined. As a result, amorphous solids are sometimes described as **supercooled liquids**, a term suggesting the kind of structural disorder found in liquids.

■ Some scientists prefer to reserve the term *solid* for crystalline substances, so they refer to amorphous solids as *supercooled liquids*.

12.12 | X-Ray Diffraction of Solids

When atoms in a crystal are bathed in X rays, they absorb some of the radiation and then emit it again in all directions. In effect, each atom becomes a tiny X-ray source. If we look at radiation from two such atoms (Figure 12.48), we find that the X rays emitted are in phase in some directions but out of phase in others. In Chapter 8 you learned that constructive (in-phase) and destructive (out-of-phase) interferences create a phenomenon called *diffraction*. X-ray diffraction by crystals has enabled many scientists to win Nobel prizes by determining the structures of extremely complex compounds in a particularly elegant way.

■ The 2009 Nobel Prize in chemistry was awarded for the X-ray structure of the ribosome, the part of a cell where proteins are formed.

In a crystal, there are enormous numbers of atoms, evenly spaced throughout the lattice. When a beam of X rays strikes a crystal, the radiation is diffracted because of constructive interference, and appears only in specific directions. In other directions, no

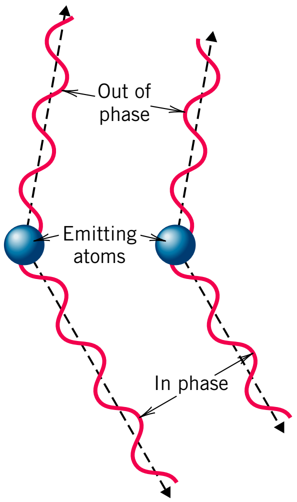


Figure 12.48 | **The diffraction of X rays from atoms in a crystal.** X rays emitted from atoms are in phase in some directions and out of phase in other directions.

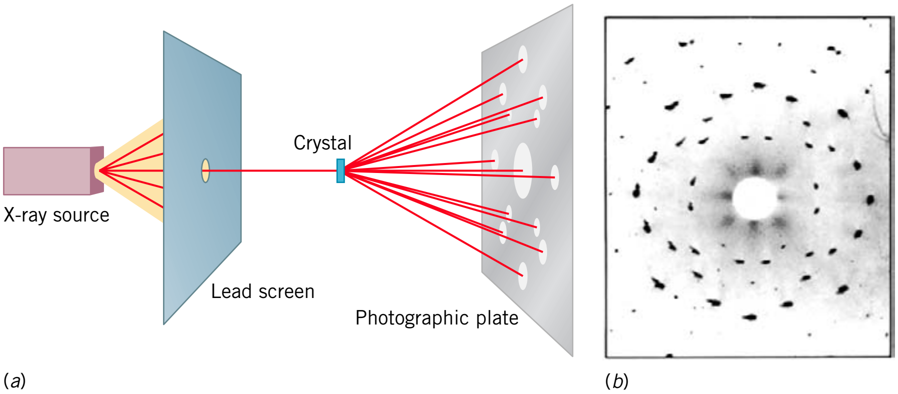


Figure 12.49 | **X-ray diffraction.** (*a*) The production of an X-ray diffraction pattern. (*b*) An X-ray diffraction pattern produced by sodium chloride recorded on photographic film. *(Visuals Unlimited)*

X rays appear because of destructive interference. When the X rays coming from the crystal fall on photographic film, the diffracted beams form a **diffraction pattern** (see Figure 12.49). The film is darkened only where the X rays strike.[4]

In 1913, the British physicist William Henry Bragg and his son William Lawrence Bragg discovered that just a few variables control the appearance of an X-ray diffraction pattern. These are shown in Figure 12.50, which illustrates the conditions necessary to obtain constructive interference of the X rays from successive layers of atoms (planes of atoms) in a crystal. A beam of X rays having a wavelength λ strikes the layers at an angle θ. Constructive interference causes an intense diffracted beam to emerge at the same angle θ. The Braggs derived an equation, now called the **Bragg equation**, relating λ, θ, and the distance between the planes of atoms, d,

TOOLS Bragg equation

$$n\lambda = 2d \sin \theta \tag{12.5}$$

where n is a whole number. The Bragg equation is the basic tool used by scientists in the study of solid structures.

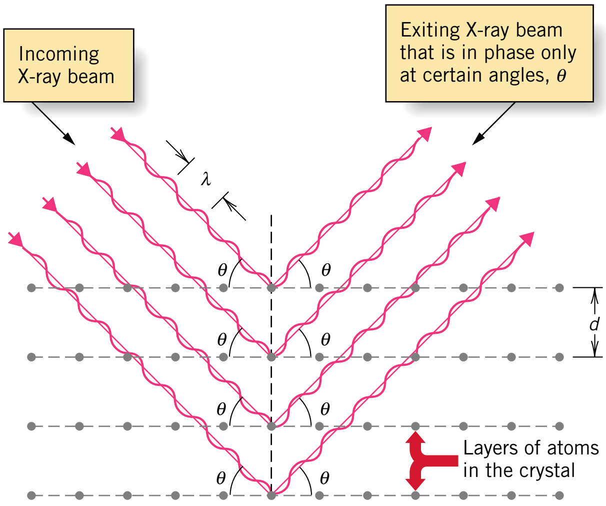

Incoming X-ray beam
Exiting X-ray beam that is in phase only at certain angles, θ
λ
θ
d
Layers of atoms in the crystal

Figure 12.50 | **The diffraction of X rays from successive layers of atoms in a crystal.** The layers of atoms are separated by a distance d. The X rays of wavelength λ enter and emerge at an angle θ relative to the layers of the atoms. For the emerging beam of X rays to have any intensity, the condition $n\lambda = 2d \sin \theta$ must be fulfilled, where n is a whole number.

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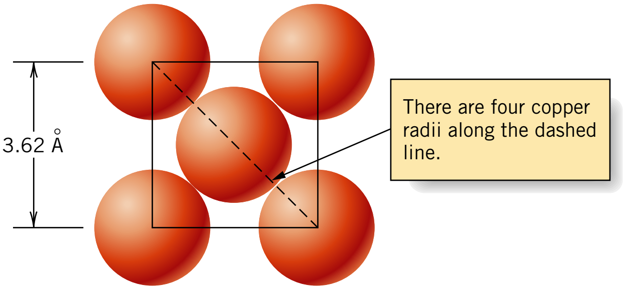
[4] Modern X-ray diffraction instruments use electronic devices to detect and measure the angles and intensities of the diffracted X rays.

To determine the structure of a crystal, the angles θ at which diffracted X-ray beams emerge from a crystal are measured. These angles are used to calculate the distances between the various planes of atoms in the crystal. The calculated interplanar distances are then used to work backward to deduce where the atoms in the crystal must be located so that layers of atoms are indeed separated by these distances. For complicated molecules and proteins, this is not a simple task, and some sophisticated mathematics as well as computers are needed to accomplish it. The efforts, however, are well rewarded because the calculations give the locations of atoms within the unit cell and the distances between them. This information, plus a lot of chemical "common sense," is used by chemists to arrive at the shapes and sizes of the molecules in the crystal. Example 12.7 illustrates how such data are used.

Example 12.7
Using Crystal Structure Data to Calculate Atomic Sizes

X-ray diffraction measurements reveal that copper crystallizes with a face-centered cubic lattice in which the unit cell length is 3.62 Å (see Figure 12.38). What is the radius of a copper atom expressed in angstroms and in picometers?

Analysis: We are given the length of the unit cell, 3.62 Å, and the shape of the unit cell, face-centered cubic. In Figure 12.38, we see that copper atoms are in contact along a diagonal (the dashed line) that runs from one corner of a face to another corner.



By geometry, we can calculate the length of this diagonal, which equals four times the radius of a copper atom. Once we calculate the radius in angstrom units we can convert to picometers.

Assembling the Tools: The two tools we will use are the arrangement of the atoms in the shape of the unit cell and the equation for determining the lengths of the sides of a right triangle, a and b, and the hypotenuse, d (the dotted line in the figure above):

$$a^2 + b^2 = d^2$$

Also, we will use the conversion factors for converting angstroms to picometers:

$$1\ \text{Å} = 1 \times 10^{-10}\ \text{m}$$
$$1\ \text{pm} = 1 \times 10^{-12}\ \text{m}$$

Solution: The unit cell is a cube, so the two sides of the triangle are the same length, l. Using the equation $a^2 + b^2 = d^2$, we can substitute l for a and b and rearrange the equation

$$l^2 + l^2 = d^2$$
$$2l^2 = d^2$$
$$\sqrt{2l^2} = d$$
$$\sqrt{2} \times l = d$$

We can now substitute in the actual length of the side of the unit cell and solve it.

$$\mathrm{d} = \sqrt{2} \times (3.62\ \text{Å}) = 5.12\ \text{Å}$$

If we call the radius of the copper atom r_{Cu}, then the diagonal equals $4 \times r_{\mathrm{Cu}}$. Therefore,

$$4 \times r_{\mathrm{Cu}} = 5.12\ \text{Å}$$
$$r_{\mathrm{Cu}} = 1.28\ \text{Å}$$

The calculated radius of the copper atom is 1.28 Å.

Next, we convert this to picometers:

$$1.28\ \cancel{\text{Å}} \times \frac{1 \times 10^{-10}\ \cancel{\mathrm{m}}}{1\ \cancel{\text{Å}}} \times \frac{1\ \mathrm{pm}}{1 \times 10^{-12}\ \cancel{\mathrm{m}}} = 128\ \mathrm{pm}$$

Is the Answer Reasonable? It's difficult to get an intuitive feel for the sizes of atoms, so we should be careful to check the calculation. The length of the diagonal seems about right; it is longer than the edge of the unit cell. If we look again at the diagram above, we can see that along the diagonal there are four copper radii. The rest of the arithmetic is okay, so our answer is correct.

12.13 | Crystal Types and Physical Properties

Solids exhibit a wide range of properties. Some, such as diamond, are very hard, whereas others, such as ice and naphthalene (moth flakes), are relatively soft. Some, such as salt crystals, have high melting points whereas others, such as candle wax, melt at low temperatures. Also, some conduct electricity, but others are nonconducting. Physical properties such as these depend on the kinds of particles in the solid as well as on the strengths of the attractive forces holding the solid together. Even though we can't make exact predictions about such properties, some generalizations do exist. In discussing them, it is convenient to divide crystals into four types: ionic, molecular, covalent, and metallic.

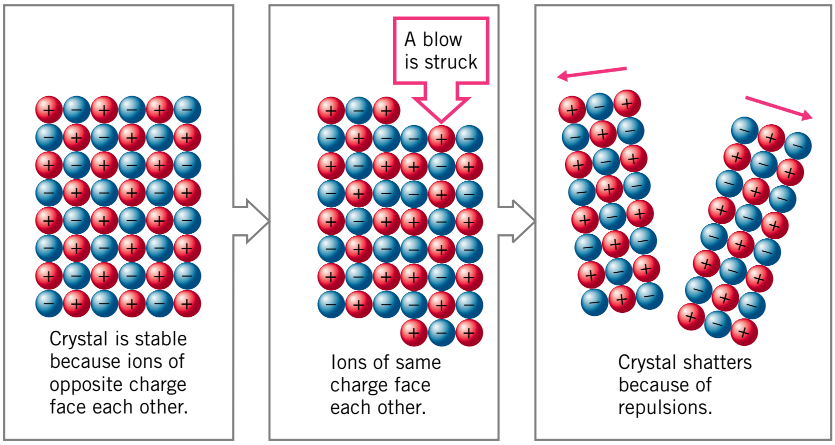
Ionic Crystals

Ionic crystals have ions at the lattice sites and the binding between them is mainly electrostatic, which is essentially non-directional. As a result, the kind of lattice formed is determined mostly by the relative sizes of the ions and their charges. When the crystal forms, the ions arrange themselves to maximize attractions and minimize repulsions.

Because electrostatic forces are strong, ionic crystals tend to be hard. They also tend to have high melting points because the ions have to be given a lot of kinetic energy to enable them to break free of the lattice and enter the liquid state. The forces between ions can also be used to explain the brittle nature of many ionic compounds. For example, when struck by a hammer, a salt crystal shatters into many small pieces. A view at the atomic level reveals how this could occur (Figure 12.51). The slight movement of a layer of ions within an ionic crystal suddenly places ions of the *same* charge next to each other, and for that instant there are large repulsive forces that split the solid.

In the solid state, ionic compounds do not conduct electricity because the charges present are not able to move. However, when melted, ionic compounds are good conductors of electricity. Melting frees the electrically charged ions to move.

Figure 12.51 | **An ionic crystal shatters when struck.** In this microview we see that striking an ionic crystal causes some of the layers to shift. This can bring ions of like charge face to face. The repulsions between the ions can then force parts of the crystal apart, causing the crystal to shatter.


A blow is struck
Crystal is stable because ions of opposite charge face each other.
Ions of same charge face each other.
Crystal shatters because of repulsions.

Molecular Crystals

■ Molecular crystals are soft because little energy is needed to separate the particles or cause them to move past each other.

Molecular crystals are solids in which the lattice sites are occupied either by atoms (as in solid argon or krypton) or by molecules (as in solid sulfur, PF_5, SO_2, or H_2O). If the molecules of such solids are relatively small, the crystals tend to be soft and have low melting points because the particles in the solid experience relatively weak intermolecular attractions. In crystals of argon, for example, the attractive forces are exclusively London forces. In SO_2, which is composed of polar molecules, there are dipole–dipole attractions as well as London forces. And, in water crystals (ice), the molecules are held in place primarily by strong hydrogen bonds. Molecular compounds do not conduct electricity either in the solid or liquid state because they are unable to transport electrical charges.

Covalent Crystals

Covalent crystals are solids in which lattice positions are occupied by atoms that are covalently bonded to other atoms at neighboring lattice sites. The result is a crystal that is essentially one gigantic molecule. These solids are sometimes called **network solids** because of the interlocking network of covalent bonds extending throughout the crystal in all directions. A typical example is diamond (see Figure 12.52). Covalent crystals tend to be very hard and to have very high melting points because of the strong attractions between covalently bonded atoms. Other examples of covalent crystals are quartz (SiO_2, found in some types of sand) and silicon carbide (SiC, a common abrasive used in sandpaper). Covalent crystals are poor conductors of electricity, although some, such as silicon, are semiconductors.

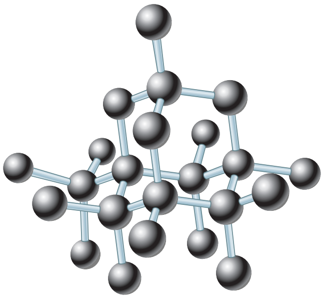


Figure 12.52 | **The structure of diamond.** Each carbon atom is covalently bonded to four others at the corners of a tetrahedron. This is just a tiny portion of a diamond; the structure extends throughout the entire diamond crystal.

Metallic Crystals

■ The band theory of solids discussed in Chapter 10 takes a close look at electronic structures of different kinds of solids.

Metallic crystals have properties that are quite different from those of the other three types. Metallic crystals conduct heat and electricity well, and they have the luster characteristically associated with metals. A number of different models have been developed to explain the properties of metals. One of the simplest models views the lattice positions of a metal lattice structure as being occupied by *positive ions* (nuclei plus core electrons). Surrounding them is a "cloud" of electrons formed by the valence electrons, which extends throughout the entire solid (see Figure 12.53). The electrons in this cloud belong to no single positive ion, but rather to the metal as a whole. Because the electrons aren't localized on any one atom, they are free to move easily, which accounts for the high electrical conductivity of metals. The electrons can also carry kinetic energy rapidly through the solid, so metals are also good conductors of heat. This model explains the luster of metals, too. When light

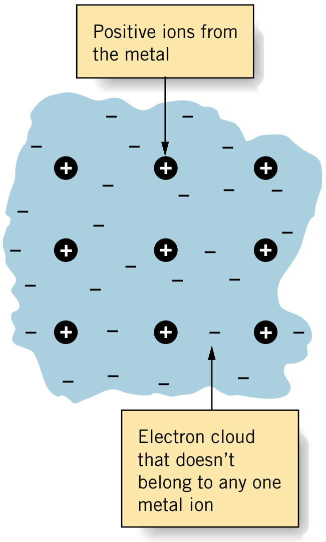

Positive ions from the metal
Electron cloud that doesn't belong to any one metal ion

Figure 12.53 | **The "electron sea" model of a metallic crystal.** In this highly simplified view of a metallic solid, metal atoms lose valence electrons to the solid as a whole and exist as positive ions surrounded by a mobile "sea" of electrons.

shines on the metal, the loosely held electrons vibrate easily and readily re-emit the light with essentially the same frequency and intensity.

Some metals, like tungsten, have very high melting points. Others, such as sodium (mp = 97.8 °C) and mercury (mp = −38.83 °C), have quite low melting points. To some extent, the melting point depends on the charge of the positive ions in the metallic crystal. The Group 1A metals have just one valence electron, so their cores are cations with a 1+ charge, which are only weakly attracted to the "electron sea" that surrounds them. Atoms of the Group 2A metals, however, form ions with a 2+ charge. These are attracted more strongly to the surrounding electron sea, so the Group 2A metals have higher melting points than their neighbors in Group 1A. Metals with very high melting points, like tungsten, must have very strong attractions between their atoms and between the atoms and the electron sea, which suggests that there probably is some covalent bonding between them as well.

The different ways of classifying crystals and a summary of their general properties are given in Table 12.7.

TOOLS

Properties of crystal types

Table 12.7 Types of Crystals

Crystal Type	Particles Occupying Lattice Sites	Type of Attractive Force	Typical Examples	Typical Properties
Ionic	Positive and negative ions	Attractions between ions of opposite charge	NaCl, $CaCl_2$, $NaNO_3$	Relatively hard; brittle; high melting points; nonconductors of electricity as solids, but conduct when melted
Molecular	Atoms or molecules	Dipole–dipole attractions, London forces, hydrogen bonding	HCl, SO_2, N_2, Ar, CH_4, H_2O	Soft; low melting points; nonconductors of electricity in both solid and liquid states
Covalent (network)	Atoms	Covalent bonds between atoms	Diamond, SiC (silicon carbide), SiO_2 (sand, quartz)	Very hard; very high melting points; nonconductors of electricity
Metallic	Positive ions	Attractions between positive ions and an electron cloud that extends throughout the crystal	Cu, Ag, Fe, Na, Hg	Range from very hard to very soft; melting points range from high to low; conduct electricity in both solid and liquid states; have characteristic luster

Example 12.8
Identifying Crystal Types from Physical Properties

The metal osmium, Os, forms an oxide with the formula OsO_4. The soft crystals of OsO_4 melt at 40 °C, and the resulting liquid does not conduct electricity. To which crystal type does solid OsO_4 probably belong?

- **Analysis:** You might be tempted to suggest that the compound is ionic simply because it is formed from a metal and a nonmetal. However, the properties of the compound are inconsistent with it being ionic. Therefore, we have to consider that there may be exceptions to the generalization discussed earlier about metal–nonmetal compounds. If so, what do the properties of OsO_4 suggest about its crystal type?

- **Assembling the Tools:** Table 12.7 lists the properties of the different types of crystals. We can use this information in the table as a tool to solve this problem.

- **Solution:** The characteristics of the OsO_4 crystals—softness and a low melting point—suggest that solid OsO_4 is a molecular solid and that it contains molecules of OsO_4. This is further supported by the fact that liquid OsO_4 does not conduct electricity, which is evidence for the lack of ions in the liquid.

- **Is the Answer Reasonable?** There's not much we can do to check ourselves here except to review our analysis.

Practice Exercises

12.19 | Stearic acid is an organic acid that has a chain of 18 carbon atoms. It is a soft solid with a melting point of 70 °C. What crystal type best describes this compound? (*Hint:* Determine the dominant attractive forces that cause stearic acid to be a solid at room temperature.)

12.20 | Boron nitride, which has the empirical formula BN, melts at 2730 °C and is almost as hard as a diamond. What is the probable crystal type for this compound?

12.21 | Crystals of elemental sulfur are easily crushed and melt at 113 °C to give a clear yellow liquid that does not conduct electricity. What is the probable crystal type for solid sulfur?

CHEMISTRY OUTSIDE THE CLASSROOM | 12.2

Giant Crystals

The most common crystals that we use are salt crystals in our salt shakers. These crystals are less than a millimeter on an edge. However, in 2000, giant gypsum crystals were discovered by miners 300 meters below the Naica mountain in Mexico. These crystals measure up to 11 meters in length and can weigh up to 55 tons. Originally, the crystals were submerged, undisturbed, in an aqueous solution of calcium sulfate at 58 °C, which allowed them to slowly grow into these gigantic forms over many thousands of years. Gypsum is unusual in that it becomes less soluble as the temperature increases. If the temperature had been cooler, the crystals would have been smaller, because more calcium sulfate would have been in solution. Since the solution was kept at such a warm temperature, however, the crystals were able to grow larger and larger as more calcium sulfate precipitated.

Another interesting aspect of this cave is that while the temperature is 58 °C, the air is between 90 and 100% humidity. Under these conditions, a person would be one of the coolest objects in the cave, since body temperature is 37 °C. Breathing this air would cause the water in the air to condense in the lungs as it cooled inside the body. A person could only stay in the cave for 10 minutes at a time without drowning.

(NG Image Collection)

Summary

Physical Properties: Gases, Liquids, and Solids. Gases expand to fill the entire volume of a container. Liquids and solids retain a constant volume if transferred from one container to another. Solids also retain a constant shape. These characteristics are related to how tightly packed the particles are and to the relative strengths of the intermolecular attractions in the different states of matter. Most physical properties depend primarily on intermolecular attractions. In gases, these attractions are weak because the molecules are so far apart. They are much stronger in liquids and solids, where the particles are packed together tightly.

Intermolecular Attractions. Polar molecules attract each other by **dipole–dipole attractions**, which arise because the positive end of one dipole attracts the negative end of another. Nonpolar molecules are attracted to each other by **London dispersion forces**, which are **instantaneous dipole–induced dipole attractions**. London forces are present between all particles, including atoms, polar and nonpolar molecules, and ions. Among different substances, London forces increase with an increase in the size of a particle's electron cloud; they also increase with increasing chain length among molecules such as the hydrocarbons. Compact molecules experience weaker London forces than similar long-chain molecules. For large molecules, the cumulative effect of large numbers of weak London force interactions can be quite strong and outweigh other intermolecular attractions. **Hydrogen bonding**, a special case of dipole–dipole attractions, occurs between molecules in which hydrogen is covalently bonded to a small, very electronegative atom—principally, nitrogen, oxygen, or fluorine. Hydrogen bonding is much stronger than the other types of intermolecular attractions. **Ion–dipole attractions** occur when ions interact with polar substances. **Ion–induced dipole attractions** result when an ion creates a dipole in a neighboring nonpolar molecule or ion.

General Properties of Liquids and Solids. Properties that depend mostly on the closeness of the packing of particles are **compressibility** (or the opposite, incompressibility) and **diffusion**. Diffusion is slow in liquids and almost nonexistent in solids at room temperature. Properties that depend mostly on the strengths of intermolecular attractions are the **retention of volume and shape, surface tension**, and the **ease of evaporation. Surface tension** is related to the energy needed to expand a liquid's surface area. A liquid can **wet** a surface if its molecules are attracted to the surface about as strongly as they are attracted to each other. The **evaporation** of liquids and solids is endothermic and produces a cooling effect. The overall rate of evaporation increases with increasing surface area. The rate of evaporation from a given surface area of a liquid increases with increasing temperature and with decreasing intermolecular attractions. The evaporation of a solid is called **sublimation**.

Changes of State. Changes from one physical state to another—namely, **fusion**, freezing, **vaporization, condensation, deposition**, or **sublimation**—can occur as dynamic equilibria. In a **dynamic equilibrium**, opposing processes occur continually at equal rates, so over time there is no apparent change in the composition of the system. For liquids and solids, equilibria are established when vaporization occurs in a sealed container. A solid is in equilibrium with its liquid at the melting point.

Vapor Pressures. When the rates of evaporation and condensation of a liquid are equal, the vapor above the liquid exerts a pressure called the **equilibrium vapor pressure** (or more commonly, just the **vapor pressure**). The vapor pressure is controlled by the rate of evaporation *per unit surface area.* When the intermolecular attractive forces are large, the rate of evaporation is small and the vapor pressure is small. Vapor pressure increases with increasing temperature because the rate of evaporation increases as the temperature rises. The vapor pressure is independent of the *total* surface area of the liquid. Solids have vapor pressures just as liquids do.

Boiling Point. A substance boils when its vapor pressure equals the prevailing atmospheric pressure. The **normal boiling point** of a liquid is the temperature at which its vapor pressure equals 1 atm. Substances with high boiling points have strong intermolecular attractions.

Energy Changes Associated with Changes of State. On a **heating curve**, flat portions correspond to phase changes in which the heat added changes the potential energies of the particles without changing their average kinetic energy. On a **cooling curve, supercooling** sometimes occurs when the temperature of the liquid drops below the freezing point of the substance. **Superheating** occurs when the temperature of a liquid rises above its boiling point. The enthalpy changes for melting, the vaporization of a liquid, and sublimation are the **molar heat of fusion**, ΔH_{fusion}, the **molar heat of vaporization**, $\Delta H_{\text{vaporization}}$, and the **molar heat of sublimation**, $\Delta H_{\text{sublimation}}$, respectively. They are all endothermic and are related in size as follows: $\Delta H_{\text{fusion}} < \Delta H_{\text{vaporization}} < \Delta H_{\text{sublimation}}$. The sizes of these enthalpy changes are large for substances with strong intermolecular attractive forces.

Heats of Vaporization and the Clausius–Clapeyron Equation. The heat of vaporization of a substance is related to the variation of the vapor pressure with changes in temperature. This is a linear relationship between the natural log of the pressure and the reciprocal of the temperature as given in the equation

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Châtelier's Principle. When the equilibrium in a system is upset by a disturbance, the system changes in a direction that minimizes the disturbance and, if possible, brings the system back to equilibrium. By this principle, we find that raising the temperature favors an endothermic change. Decreasing the volume favors a change toward a more dense phase.

Phase Diagrams. Temperatures and pressures at which equilibria can exist between phases are depicted graphically in a **phase diagram**. The three equilibrium lines intersect at the **triple point**. The liquid–vapor line terminates at the **critical point**. At the **critical temperature**, a liquid has a vapor pressure equal to its **critical pressure**. Above the critical temperature a liquid phase cannot be formed; the single phase that exists is called a **supercritical fluid**. The equilibrium lines also divide a phase diagram into temperature–pressure regions in which a substance can exist in just a single phase. Water is different from most substances in that its melting point decreases with increasing pressure.

Crystalline Solids. Crystalline solids have highly ordered arrangements of particles within them, which can be described in terms of repeating three-dimensional arrays of points called **lattices**. The simplest portion of a lattice is its **unit cell**. Many structures can be described with the same lattice by associating different units (i.e., atoms, molecules, or ions) to lattice points and by changing the dimensions of the unit cell. All crystals can be classified into one of the 14 different lattice types shown in Table 12.6. Three cubic unit cells are possible—**simple cubic, face-centered cubic**, and **body-centered cubic**. Sodium chloride and many other alkali metal halides crystallize in the **rock salt structure**, which contains four formula units per unit cell. Two modes of closest packing of atoms are **cubic closest packing (ccp)** and **hexagonal closest packing (hcp)**. The ccp structure has an A-B-C-A-B-C- . . . alternating stacking of layers of spheres; the hcp structure has an A-B-A-B- . . . stacking of layers. **Amorphous** solids lack the internal structure of crystalline solids. Glass is an amorphous solid and is sometimes called a **supercooled liquid**.

X-Ray Diffraction. Information about crystal structures is obtained experimentally from **X-ray diffraction patterns** produced by the constructive and destructive interference of X rays scattered by atoms. Distances between planes of atoms in a crystal can be calculated by the Bragg equation, $n\lambda = 2d \sin \theta$, where n is a whole number, λ is the wavelength of the X rays, d is the distance between planes of atoms producing the diffracted beam, and θ is the angle at which the diffracted X-ray beam emerges relative to the planes of atoms producing the diffracted beam.

Crystal Types. Crystals can be divided into four general types: **ionic, molecular, covalent**, and **metallic**. Their properties depend on the kinds of particles within the lattice and on the attractions between the particles, as summarized in Table 12.7.

TOOLS

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Types of intermolecular forces (page 535)

London forces, dipole–dipole interactions, and hydrogen bonding are the three intermolecular forces that are responsible for the intermolecular attractions between molecules in the liquid and solid states. Ion–dipole and ion–induced dipole attractions are the interactions of ions with polar and nonpolar substances. See the summary table on page 535. From molecular structure, we can determine whether a molecule is polar or not and whether it has N—H or O—H bonds. This lets us predict and compare the strengths of intermolecular attractions.

Factors that affect the rate of evaporation: temperature and intermolecular forces (page 542)

As the temperature of a substance increases, the average kinetic energy of the molecules in the substance increases, and the rate of evaporation increases. The stronger the intermolecular forces, the slower is the rate of evaporation.

Factors that affect vapor pressure (page 545)

The two factors that affect the vapor pressure of a substance are the temperature of the system and the intermolecular forces. Therefore, we can compare the strengths of the intermolecular forces based on the relative magnitudes of the vapor pressures at a given temperature. The amount of substance present and the volume of the space for the vapor do not affect the vapor pressure as long as some of the liquid or solid is present.

Boiling points and intermolecular forces (page 547)

These allow us to compare the strengths of intermolecular forces in substances based on their boiling points. The normal boiling point of a liquid is the boiling point of the liquid at 1 atm.

Enthalpy changes during phase changes (page 549)

These changes allow us to compare the strengths of intermolecular forces in substances based on relative values of $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.

Heat of fusion (page 550)
The amount of heat required to melt a given amount of a substance is given by

$$q = n \times \Delta H_{\text{fusion}}$$

Clausius–Clapeyron equation (page 553)
The relationship between vapor pressure, heats of vaporization, and temperature is

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Châtelier's principle (page 555)
Le Châtelier's principle enables us to predict the direction in which the position of equilibrium is shifted when a dynamic equilibrium is upset by a disturbance. You should be able to predict how the position of equilibrium between phases is affected by temperature and pressure changes.

Phase diagrams (page 556)
We use a phase diagram to identify temperatures and pressures at which equilibrium can exist between phases of a substance, and to identify conditions under which only a single phase can exist.

Cubic unit cells (page 562)
The three basic cubic lattice structures are simple cubic, face-centered cubic, and body-centered cubic. By knowing the arrangements of atoms in these unit cells, we can use the dimensions of the unit cell to calculate atomic radii and other properties.

Counting atoms in unit cells (page 562)
The stoichiometry of the atoms in the unit cell must equal the stoichiometry of the compound. The number of atoms in the unit cell can be counted by adding up the parts of the atoms that are contained in the unit cell: $\frac{1}{8}$ for an atom in a corner, $\frac{1}{4}$ for an atom on an edge, $\frac{1}{2}$ for an atom in a face, and 1 for an atom wholly in the unit cell.

Bragg equation (page 569)

$$n\lambda = 2d \sin \theta$$

Using the wavelength of X rays and the angles at which X rays are diffracted from a crystal, the distances between planes of atoms can be calculated.

Properties of crystal types (page 573)
By examining certain physical properties of a solid (i.e., the hardness, melting point, and electrical conductivity in the solid and liquid states), we can often predict the nature of the particles that occupy lattice sites in the solid and the kinds of attractive forces between them.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Comparisons among the States of Matter

12.1 Why are the intermolecular attractive forces stronger in liquids and solids than they are in gases?

12.2 Compare the behavior of gases, liquids, and solids when they are transferred from one container to another.

12.3 For a given substance, how do the intermolecular attractive forces compare in its gaseous, liquid, and solid states?

12.4 Why do intermolecular attractions weaken as the distances between the molecules increase?

Intermolecular Attractions

12.5 Which kinds of attractive forces, intermolecular or intramolecular, are responsible for chemical properties? Which kind are responsible for physical properties?

12.6 What are *London forces*? How are they affected by the sizes of the atoms in a molecule? How are they affected by the number of atoms in a molecule? How are they affected by the shape of a molecule?

12.7 Define *polarizability*. How does this property affect the strengths of London forces?

12.8 Describe *dipole–dipole attractions*.

12.9 Which nonmetals, besides hydrogen, are most often involved in hydrogen bonding? Why these elements and not others?

12.10 Which is expected to have the higher boiling point, C_8H_{18} or C_4H_{10}? Explain your choice.

12.11 Ethanol and dimethyl ether have the same molecular formula, C_2H_6O. Ethanol boils at 78.4 °C, whereas dimethyl ether boils at −23.7 °C. Their structural formulas are

CH_3CH_2OH	CH_3OCH_3
ethanol	dimethyl ether

Explain why the boiling point of the ether is so much lower than the boiling point of ethanol.

12.12 How do the strengths of covalent bonds and dipole–dipole attractions compare? How do the strengths of ordinary dipole–dipole attractions compare with the strengths of hydrogen bonds?

12.13 Which would give a stronger ion–dipole interaction with water molecules: Al^{3+} or Na^+?

12.14 For each pair, which ion produces the stronger ion-induced dipole attractions with oxygen molecules?

(a) O^{2-} or S^{2-}, **(b)** Mg^{2+} or Al^{3+}

General Properties of Liquids and Solids

12.15 Name two physical properties of liquids and solids that are controlled primarily by how tightly packed the particles are. Name three that are controlled mostly by the strengths of the intermolecular attractions.

12.16 Why does diffusion occur more slowly in liquids than in gases? Why does diffusion occur extremely slowly in solids?

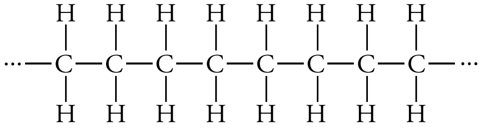
12.17 On the basis of kinetic theory, would you expect the rate of diffusion in a liquid to increase or decrease as the temperature is increased? Explain your answer.

12.18 What is *surface tension*? Why do molecules at the surface of a liquid behave differently from those within the interior?

12.19 Which liquid is expected to have the larger surface tension at a given temperature, CCl_4 or H_2O? Explain your answer.

12.20 What does *wetting* of a surface mean? What is a *surfactant?* What is its purpose and how does it function?

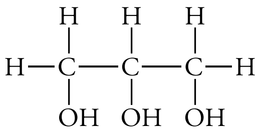
12.21 Polyethylene plastic consists of long chains of carbon atoms, each of which is also bonded to hydrogens, as shown in the following structure:



$$\cdots-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\cdots$$

Water forms beads when placed on a polyethylene surface. Why?

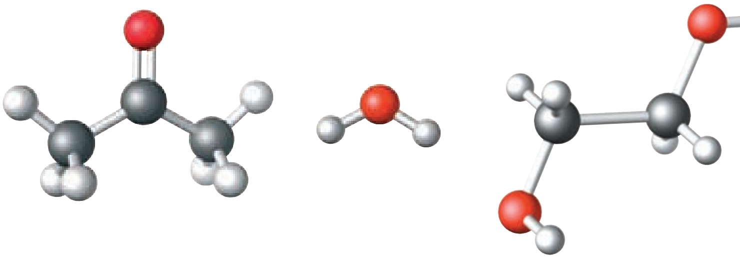
12.22 The structural formula for glycerol is



$$\mathrm{H}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$$

Would you expect this liquid to wet glass surfaces? Explain your answer.

12.23 Acetone (CH_3COCH_3), water, and ethylene glycol (CH_2OHCH_2OH) are listed here, and shown below in ball-and-stick figures, in the order of increasing viscosity for these three compounds. Why is this the correct order?



12.24 On the basis of what happens on the molecular level, why does evaporation lower the temperature of a liquid?

12.25 On the basis of the distribution of kinetic energies of the molecules of a liquid, explain why increasing the liquid's temperature increases the rate of evaporation.

12.26 How is the rate of evaporation of a liquid affected by increasing the surface area of the liquid? How is the rate of evaporation affected by the strengths of intermolecular attractive forces?

12.27 During the cold winter months, snow often disappears gradually without melting. How is this possible? What is the name of the process responsible for this phenomenon?

Changes of State and Equilibrium

12.28 What terms do we use to describe the following changes of state?

(a) solid → gas,
(b) gas → solid,
(c) liquid → gas,
(d) gas → liquid,
(e) solid → liquid,
(f) liquid → solid

12.29 When a molecule escapes from the surface of a liquid by evaporation, it has a kinetic energy that's much larger than the average KE. Why is it likely that after being in the vapor for a while its kinetic energy will be much less? If this molecule collides with the surface of the liquid, is it likely to bounce out again?

12.30 Why does a molecule of a vapor that collides with the surface of a liquid tend to be captured by the liquid, even if the incoming molecule has a large kinetic energy?

12.31 When an equilibrium is established in the evaporation of a liquid into a sealed container, we refer to it as a *dynamic equilibrium*. Why?

12.32 Viewed at the molecular level, what is happening when a dynamic equilibrium is established between the liquid and solid forms of a substance? What is the temperature called at which there is an equilibrium between a liquid and a solid?

12.33 Is it possible to establish an equilibrium between a solid and its vapor? Explain.

Vapor Pressure

12.34 Define *equilibrium vapor pressure.* Why do we call the equilibrium involved a *dynamic equilibrium*?

12.35 Explain why changing the volume of a container in which there is a liquid–vapor equilibrium has no effect on the equilibrium vapor pressure.

12.36 Why doesn't a change in the surface area of a liquid cause a change in the equilibrium vapor pressure?

12.37 What effect does increasing the temperature have on the equilibrium vapor pressure of a liquid? Why?

12.38 Why does moisture condense on the outside of a cool glass of water in the summertime?

12.39 Why do we feel more uncomfortable in humid air at 90 °F than in dry air at 90 °F?

Boiling Points of Liquids

12.40 Define *boiling point* and *normal boiling point.*

12.41 Why does the boiling point vary with atmospheric pressure?

12.42 Mt. Kilimanjaro in Tanzania is the tallest peak in Africa (19,340 ft). The normal barometric pressure at the top of this mountain is about 345 torr. At what Celsius temperature would water be expected to boil there? (See Figure 12.29.)

12.43 When liquid ethanol begins to boil, what is present inside the bubbles that form?

12.44 The radiator cap of an automobile engine is designed to maintain a pressure of approximately 15 lb/in.^{2} above normal atmospheric pressure. How does this help prevent the engine from "boiling over" in hot weather?

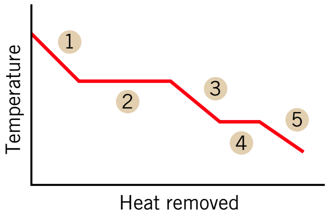
12.45 Butane, C_4H_{10}, has a boiling point of -0.5 °C (which is 31 °F). Despite this, liquid butane can be seen sloshing about inside a typical butane lighter, even at room temperature. Why isn't the butane boiling inside the lighter at room temperature?

12.46 Why does H_2S have a lower boiling point than H_2Se? Why does H_2O have a much higher boiling point than H_2S?

12.47 An H—F bond is more polar than an O—H bond, so HF forms stronger hydrogen bonds than H_2O. Nevertheless, HF has a lower boiling point than H_2O. Explain why this is so.

Energy Changes that Accompany Changes of State

12.48 The following is a cooling curve for one mole of a substance:



(a) On which portions of this graph do we find the average kinetic energy of the molecules of the substance changing?

(b) On which portions of this graph is the amount of heat removed related primarily to a lowering of the potential energy of the molecules?

(c) Which portion of the graph corresponds to the release of the heat of vaporization?

(d) Which portion of the graph corresponds to the release of the heat of fusion?

(e) Which is larger: the heat of fusion or the heat of vaporization?

(f) On the graph, indicate the melting point of the solid.

(g) On the graph, indicate the boiling point of the liquid.

(h) On the drawing, indicate how supercooling of the liquid would affect the graph.

12.49 Why is $\Delta H_{\text{vaporization}}$ larger than ΔH_{fusion}? How does $\Delta H_{\text{sublimation}}$ compare with $\Delta H_{\text{vaporization}}$? Explain your answer.

12.50 Would the "heat of condensation," $\Delta H_{\text{condensation}}$, be exothermic or endothermic?

12.51 Hurricanes can travel for thousands of miles over warm water, but they rapidly lose their strength when they move over a large land mass or over cold water. Why?

12.52 Ethanol (grain alcohol) has a molar heat of vaporization of 39.3 kJ/mol. Ethyl acetate, a common solvent, has a molar heat of vaporization of 32.5 kJ/mol. Which of these substances has the larger intermolecular attractions?

12.53 A burn caused by steam is much more serious than one caused by the same amount of boiling water. Why?

12.54 Arrange the following substances in order of their increasing values of $\Delta H_{\text{vaporization}}$: **(a)** HF, **(b)** CH_4, **(c)** CF_4, **(d)** HCl.

Clausius–Clapeyron Equation

12.55 According to the Clausius–Clapeyron equation, how does the vapor pressure of a substance change as the temperature increases?

12.56 Why can't Celsius temperatures be used in the Clausius–Clapeyron equation?

Le Châtelier's Principle

12.57 State Le Châtelier's principle in your own words.

12.58 What do we mean by the *position of equilibrium*?

12.59 Use Le Châtelier's principle to predict the effect of adding heat in the equilibrium: solid + heat $\rightleftharpoons$ liquid.

12.60 Use Le Châtelier's principle to explain why lowering the temperature lowers the vapor pressure of a solid.

Phase Diagrams

12.61 For most substances, the solid is more dense than the liquid. Use Le Châtelier's principle to explain why the melting point of such substances should *increase* with increasing pressure. Sketch the phase diagram for such a substance, being sure to have the solid–liquid equilibrium line slope in the correct direction.

12.62 Define *critical temperature* and *critical pressure.*

12.63 What is a supercritical fluid? Why is supercritical CO_2 used to decaffeinate coffee?

12.64 What phases of a substance are in equilibrium at the triple point?

12.65 Why doesn't CO_2 have a normal boiling point?

12.66 At room temperature, hydrogen can be compressed to very high pressures without liquefying. On the other hand, butane becomes a liquid at high pressure (at room temperature). What does this tell us about the critical temperatures of hydrogen and butane?

Crystalline Solids and X-Ray Diffraction

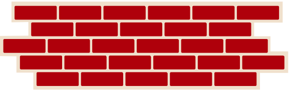
12.67 What is the difference between a crystalline solid and an amorphous solid?

12.68 What is a *lattice*? What is a *unit cell*?

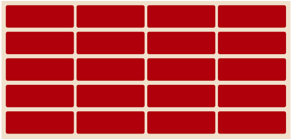
12.69 What relationship is there between a crystal lattice and its unit cell?

12.70 The diagrams that follow illustrate two typical arrangements of paving bricks in a patio or driveway. Sketch the unit cell that corresponds to each pattern of bricks.

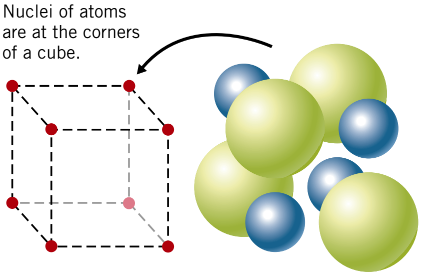
(*a*)



(*b*)



12.71 The figure below illustrates the way the atoms of two different elements are packed in a certain solid. The nuclei occupy positions at the corners of a cube. Is this cube the unit cell for this substance? Explain your answer.



12.72 Make a sketch of a layer of sodium ions and chloride ions in a NaCl crystal. Indicate how the ions are arranged in a face-centered cubic pattern, regardless of whether we place lattice points at the Cl^- ions or the Na^+ ions.

12.73 How do the crystal structures of copper and gold differ? In what way are they similar? On the basis of the locations of the elements in the periodic table, what kind of crystal structure would you expect for silver?

12.74 What kind of lattice does zinc sulfide have? What kind of lattice does calcium fluoride have?

12.75 Only 14 different kinds of crystal lattices are possible. How can this be true, considering the fact that there are millions of different chemical compounds that are able to form crystals?

12.76 Write the Bragg equation and define the symbols.

12.77 Why can't $CaCl_2$ or $AlCl_3$ form crystals with the same structure as NaCl?

Crystal Types

12.78 What kinds of particles are located at the lattice sites in a metallic crystal?

12.79 What kinds of attractive forces exist between particles in **(a)** molecular crystals, **(b)** ionic crystals, and **(c)** covalent crystals?

12.80 Why are covalent crystals sometimes called *network solids*?

Amorphous Solids

12.81 What does the word *amorphous* mean?

12.82 What is an amorphous solid? Compare what happens when crystalline and amorphous solids are broken into pieces.

Review Problems

Intermolecular Attractions and Molecular Structure

12.83 Which liquid evaporates faster at 25 °C, diethyl ether (an anesthetic) or butanol (a solvent used in the preparation of shellac and varnishes)? Both have the molecular formula $C_4H_{10}O$, but their structural formulas are different:

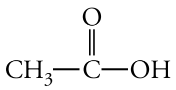
$CH_3CH_2CH_2CH_2OH$ (butanol) $\quad$ $CH_3CH_2{-}O{-}CH_2CH_3$ (diethyl ether)

OH **12.84** Which compound should have the higher vapor pressure at 25 °C, butanol or diethyl ether? Which should have the higher boiling point?

12.85 What kinds of intermolecular attractive forces (i.e., dipole–dipole, London, and hydrogen bonding) are present in the following substances?

(a) HF **(b)** PCl_3 **(c)** SF_6 **(d)** SO_2

12.86 What kinds of intermolecular attractive forces are present in the following substances?

(a) 
$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH$

(b) H_2S

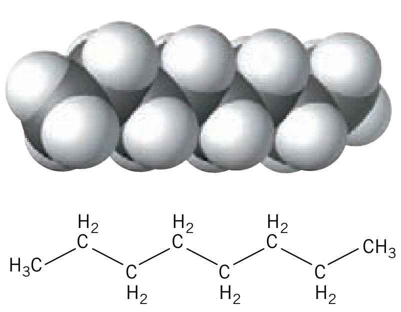
(c) SO_3

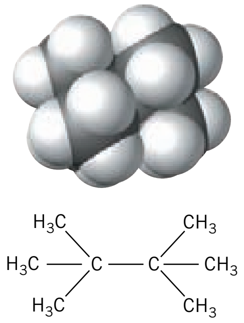
(d) CH_3NH_2

OH **12.87** Consider the compounds $CHCl_3$ (chloroform, an important solvent that was once used as an anesthetic) and $CHBr_3$ (bromoform, which has been used as a sedative). Compare the strengths of their dipole–dipole attractions and the strengths of their London forces. Their boiling points are 61 °C and 149 °C, respectively. For these compounds, which kinds of attractive forces (i.e., dipole–dipole or London) are more important in determining their boiling points? Justify your answer.

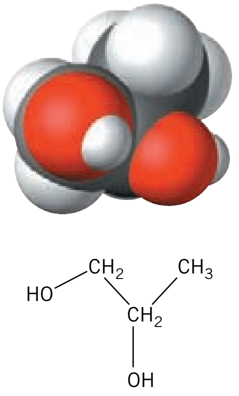
12.88 Carbon dioxide does not liquefy at atmospheric pressure, but instead forms a solid that sublimes at −78 °C. Nitrogen dioxide forms a liquid that boils at 21 °C at atmospheric pressure. How do these data support the statement that CO_2 is a linear molecule whereas NO_2 is nonlinear?

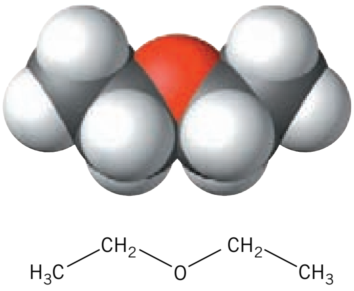
12.89 Which of the following isomers of octane should have the higher viscosity?





12.90 Which molecule below will wet a greasy glass surface more effectively, propylene glycol (left) or diethyl ether (right).





12.91 Which should have the higher boiling point, ethanol (CH_3CH_2OH, found in alcoholic beverages) or ethanethiol (CH_3CH_2SH, a foul-smelling liquid found in the urine of rabbits that have feasted on cabbage)?

12.92 How do the strengths of London forces compare in $CO_2(l)$ and $CS_2(l)$? Which of these is expected to have the higher boiling point? (Check your answer by referring to the *Handbook of Chemistry and Physics*, which is available in your school library.)

OH **12.93** The following are the vapor pressures of some relatively common chemicals measured at 20 °C:

Benzene, C_6H_6	80 torr
Acetic acid, $HC_2H_3O_2$	11.7 torr
Acetone, C_3H_6O	184.8 torr
Diethyl ether, $C_4H_{10}O$	442.2 torr
Water	17.5 torr

Arrange these substances in order of increasing intermolecular attractive forces.

12.94 The boiling points of some common substances are as follows:

Ethanol, C_2H_5OH	78.4 °C
Ethylene glycol, $C_2H_4(OH)_2$	197.2 °C
Water	100 °C
Diethyl ether, $C_4H_{10}O$	34.5 °C

Arrange these substances in order of increasing strengths of intermolecular attractions.

12.95 What intermolecular forces must the following substances overcome in the process of vaporization? **(a)** ethanol (C_2H_5OH), **(b)** acetonitrile (H_3CCN), and **(c)** sodium chloride (NaCl)?

12.96 What intermolecular attractions will be formed when the following substances condense from the gas phase? **(a)** hexane (C_6H_{14}), **(b)** acetone (H_3CCOCH_3), and **(c)** argon?

Energy Changes that Accompany Changes of State

OH **12.97** The molar heat of vaporization of water at 25 °C is +43.9 kJ/mol. How many kilojoules of heat would be required to vaporize 125 mL (0.125 kg) of water?

12.98 The molar heat of vaporization of acetone, C_3H_6O, is 30.3 kJ/mol at its boiling point. How many kilojoules of heat would be liberated by the condensation of 5.00 g of acetone?

12.99 Suppose 45.0 g of water at 85 °C is added to 105.0 g of ice at 0.0 °C. The molar heat of fusion of water is 6.01 kJ/mol, and the specific heat of water is 4.18 J/g °C. On the basis of these data, **(a)** what will be the final temperature of the mixture and **(b)** how many grams of ice will melt?

12.100 A cube of solid benzene (C_6H_6) at its melting point and weighing 10.0 g is placed in 10.0 g of water at 35 °C. Given that the heat of fusion of benzene is 9.92 kJ/mol, to what temperature will the water have cooled by the time all of the benzene has melted?

Heats of Vaporization

12.101 Mercury is used in barometers since it has such a low vapor pressure. The heat of vaporization of mercury is 59.2 kJ mol^{-1}, and its normal boiling point is 629.9 K. What is the vapor pressure of mercury at 298.2 K?

12.102 The heat of vaporization of water is 43.9 kJ mol^{-1}, and its normal boiling point is 373 K. Estimate the vapor pressure of water at 351 K.

12.103 We can determine the heat of vaporization by using the Clausius–Clapeyron equation if we know the vapor pressures of a substance at two different temperatures. Determine the heat of vaporization of diethyl ether if the vapor pressure is 1.0 mm Hg at −74.3 °C and 425 mm Hg at 18.7 °C.

12.104 If the vapor pressure of ethylene glycol is 7.23 mm Hg at 95.1 °C and 755 mm Hg at 197.1 °C, what is the heat of vaporization of ethylene glycol?

Phase Diagrams

12.105 Sketch the phase diagram for a substance that has a triple point at −15.0 °C and 0.30 atm, melts at −10.0 °C at 1 atm, and has a normal boiling point of 90 °C.

12.106 Based on the phase diagram sketched in Problem 12.105, below what pressure will the substance undergo sublimation? How does the density of the liquid compare with the density of the solid?

12.107 According to Figure 12.31, what phase(s) should exist for CO_2 at **(a)** −60 °C and 6 atm, **(b)** −60 °C and 2 atm, **(c)** −40 °C and 10 atm, and **(d)** −57 °C and 5.2 atm?

OH **12.108** Looking at the phase diagram for CO_2 (Figure 12.31), how can we tell that solid CO_2 is more dense than liquid CO_2?

Crystalline Solids and X-Ray Diffraction

12.109 How many zinc and sulfide ions are present in the unit cell of zinc sulfide? (See Figure 12.42.)

12.110 How many copper atoms are within the face-centered cubic unit cell of copper? (*Hint:* See Figure 12.38 and add up all of the *parts* of atoms in the fcc unit cell.)

OH ILW **12.111** The atomic radius of nickel is 1.24 Å. Nickel crystallizes in a face-centered cubic lattice. What is the length of the edge of the unit cell expressed in angstroms and in picometers?

12.112 Silver forms face-centered cubic crystals. The atomic radius of a silver atom is 144 pm. Draw the face of a unit cell with the nuclei of the silver atoms at the lattice points. The atoms are in contact along the diagonal. Calculate the length of an edge of this unit cell.

12.113 Potassium ions have a radius of 133 pm, and bromide ions have a radius of 195 pm. The crystal structure of potassium bromide is the same as for sodium chloride. Estimate the length of the edge of the unit cell in potassium bromide.

12.114 The unit cell edge in sodium chloride has a length of 564.0 pm. The sodium ion has a radius of 95 pm. What is the *diameter* of a chloride ion?

OH **12.115** Calculate the angles at which X rays of wavelength 229 pm will be observed to be defracted from crystal planes spaced **(a)** 1.0×10^3 pm apart and **(b)** 2.5×10^2 pm apart. Assume $n = 1$ for both calculations.

12.116 Calculate the interplanar spacings (in picometers) that correspond to defracted beams of X rays at $\theta = 20.0°$, 27.4°, and 35.8°, if the X rays have a wavelength of 141 pm. Assume that $n = 1$.

12.117 Cesium chloride forms a simple cubic lattice in which Cs^+ ions are at the corners and a Cl^- ion is in the center (see Figure 12.41). The cation–anion contact occurs along the *body diagonal* of the unit cell. (The body diagonal starts at one corner and then runs through the center of the cell to the opposite corner.). The length of the edge of the unit cell is 412.3 pm. The Cl^- ion has a radius of 181 pm. Calculate the radius of the Cs^+ ion.

12.118 Rubidium chloride has the rock salt structure. Cations and anions are in contact along the edge of the unit cell, which is 658 pm long. The radius of the chloride ion is 181 pm. What is the radius of the Rb^+ ion?

Crystal Types

12.119 Tin(IV) chloride, $SnCl_4$, has soft crystals with a melting point of −30.2 °C. The liquid is nonconducting. What type of crystal is formed by $SnCl_4$?

12.120 Elemental boron is a semiconductor, is very hard, and has a melting point of about 2250 °C. What type of crystal is formed by boron?

12.121 Columbium is another name for one of the elements. This element is shiny, soft, and ductile. It melts at 2468 °C, and the solid conducts electricity. What kind of solid does columbium form?

12.122 Elemental phosphorus consists of soft white "waxy" crystals that are easily crushed and melt at 44 °C. The solid does not conduct electricity. What type of crystal does phosphorus form?

12.123 Indicate which type of crystal (i.e., ionic, molecular, covalent, or metallic) each of the following would form when it solidifies: **(a)** Br_2, **(b)** LiF, **(c)** MgO, **(d)** Mo, **(e)** Si, **(f)** PH_3, and **(g)** NaOH.

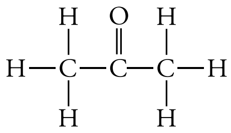
12.124 Indicate which type of crystal (i.e., ionic, molecular, covalent, or metallic) each of the following would form when it solidifies: **(a)** O_2, **(b)** H_2S, **(c)** Pt, **(d)** KCl, **(e)** Ge, **(f)** $Al_2(SO_4)_3$, and **(g)** Ne.

Additional Exercises

12.125 List *all* of the attractive forces that exist in solid Na_2SO_3.

OH **12.126** Calculate the mass of water vapor present in 10.0 L of air at 20.0 °C if the relative humidity is 75%.

12.127 Should acetone molecules be attracted to water molecules more strongly than to other acetone molecules? Explain your answer. The structure of acetone is as follows:



$$\mathrm{H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H}$$

OH **12.128** Acetic acid has a heat of fusion of 10.8 kJ/mol and a heat of vaporization of 24.3 kJ/mol.

$$\begin{aligned} &HC_2H_3O_2(s) \rightarrow HC_2H_3O_2(l) && \Delta H_{\text{fusion}} = 10.8 \text{ kJ/mol} \\ &HC_2H_3O_2(l) \rightarrow HC_2H_3O_2(g) && \Delta H_{\text{vaporization}} = 24.3 \text{ kJ/mol} \end{aligned}$$

Use Hess's law to estimate the value for the heat of sublimation of acetic acid in kilojoules per mole.

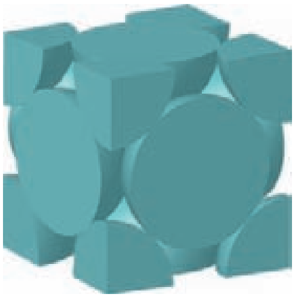
***12.129** Melting point is sometimes used as an indication of the extent of ionic bonding in a compound—the higher the melting point, the more ionic the substance. On this basis, oxides of metals seem to become less ionic as the charge on the metal ion increases. Thus, Cr_2O_3 has a melting point of 2266 °C whereas CrO_3 has a melting point of only 196 °C. The explanation often given is similar in some respects to explanations of the variations in the strengths of certain intermolecular attractions given in this chapter. Provide an explanation for the greater degree of electron sharing in CrO_3 as compared with Cr_2O_3.

***12.130** When warm, moist air sweeps in from the ocean and rises over a mountain range, it expands and cools. Explain how this cooling is related to the attractive forces between gas molecules. Why does this cause rain to form? When the air drops down the far side of the range, its pressure rises as it is compressed. Explain why this causes the air temperature to rise. How does the humidity of this air compare with the air that originally came in off the ocean? Now explain why the coast of California is lush farmland, whereas valleys (such as Death Valley) that lie to the east of the tall Sierra Nevada mountains are arid and dry.

12.131 Gold crystallizes in a face-centered cubic lattice. The edge of the unit cell has a length of 407.86 pm. The density of gold is 19.31 g/cm³. Use these data and the atomic mass of gold to calculate the value of Avogadro's number.

OH ***12.132** Gold crystallizes with a face-centered cubic unit cell with an edge length of 407.86 pm. Calculate the atomic radius of gold in units of picometers.

12.133 Identify the type of unit cell belonging to the following structures:



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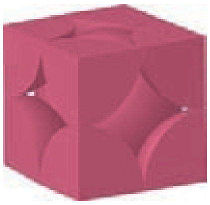

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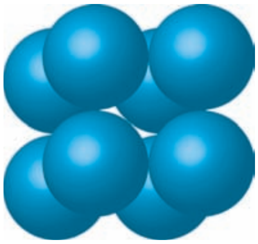


(*c*)

***12.134** Calculate the amount of empty space (in pm³) in simple cubic, body-centered cubic, and face-centered cubic unit cells if the lattice points are occupied by identical atoms with a diameter of 1.00 pm. Which of these structures gives the most efficient packing of atoms?

12.135 Silver has an atomic radius of 144 pm. What would be the density of silver in g cm^{-3} if it were to crystallize in **(a)** a simple cubic lattice, **(b)** a body-centered cubic lattice, and **(c)** a face-centered cubic lattice? The actual density of silver is 10.6 g cm^{-3}. Which cubic lattice does silver have?

***12.136** Potassium chloride crystallizes with the rock salt structure. When bathed in X rays, the layers of atoms corresponding to the surfaces of the unit cell produce a diffracted beam of X rays at an angle of 12.8°. Calculate the density of KCl.

12.137 Why do clouds form when the humid air of a weather system called a *warm front* encounters the cool, relatively dry air of a *cold front*?

| Multi-Concept Problems

***12.138** There are 270 Calories in a Hershey's® Milk Chocolate bar. If all of the energy in the bar were used to heat up 75 mL of ice at -25 °C, how hot would the water get? What state would the water be in? The following data might be useful: $\Delta H_{\text{vap}} = 43.9$ kJ/mol, $\Delta H_{\text{fusion}} = 6.02$ kJ/mol, $\Delta H_{\text{sublimation}} = 49.9$ kJ/mol, specific heat of ice $= 2.05$ J g^{-1} °C^{-1}, specific heat of water $= 4.18$ J g^{-1} °C^{-1}, and specific heat of steam $= 2.08$ J g^{-1} °C^{-1}. Assume that the specific heat of water does not change with temperature.

***12.139** Freeze-drying is a process used to preserve food. If strawberries are to be freeze-dried, then they would be frozen to -80 °C and subjected to a vacuum of 0.001 torr. As the water is removed, it is frozen to a cold surface in the freeze-drier. If 150 mL of water has to be removed from a batch of strawberries, how much energy would be required? What changes of state are taking place? At any given time, how much water is in the atmosphere if the volume of the freeze-drier is 5 liters? If it takes one hour to remove one mL of water, how long will it take to freeze-dry the strawberries?

| Exercises in Critical Thinking

12.140 Supercritical CO_2 is used to decaffeinate coffee. Propose other uses for supercritical fluids.

12.141 Freshly precipitated crystals are usually very small. Over time the crystals tend to grow larger. How can we use the concept of dynamic equilibrium to explain this phenomenon?

12.142 What are some "everyday" applications of Le Châtelier's principle? For example, we turn up the heat in an oven to cook a meal faster.

12.143 Lubricants, oils, greases, and so on are very important in everyday life. Explain how a lubricant works in terms of intermolecular forces.

12.144 Galileo's thermometer is a tube of liquid that has brightly colored glass spheres that float or sink depending on the temperature. Using your knowledge from the past two chapters, explain all of the processes that are involved in this thermometer.

12.145 Use the Clausius–Clapeyron equation to plot the vapor pressure curve of a gas that has a heat of vaporization of 21.7 kJ mol^{-1} and a boiling point of 48 °C. Compare your results to the other vapor pressure curves in this chapter.

12.146 Will the near weightless environment of the international space station have any effect on intermolecular forces and chemical reactions? What types of chemical reactions may benefit from a weightless environment?

13

Mixtures at the Molecular Level: Properties of Solutions

Chapter Outline

13.1 | Intermolecular Forces and the Formation of Solutions

13.2 | Heats of Solution

13.3 | Solubility as a Function of Temperature

13.4 | Henry's Law

13.5 | Temperature-Independent Concentration Units

13.6 | Temperature-Dependent Concentration Units

13.7 | Colligative Properties

13.8 | Heterogeneous Mixtures

It is a relatively rare event to encounter a pure substance. Most things we see, purchase and use are mixtures that are either homogeneous or heterogeneous. On the grocery shelf in our photo, we observe an array of products that are obviously mixtures. Some of the bottles contain Italian salad dressing which is definitely a heterogeneous mixture. Other bottles contain mixtures that we can consider to be homogeneous solutions. In this chapter we expand upon the fundamental properties of pure gases, liquids and solids that we developed in Chapters 11 and 12 to consider what happens when we make homogeneous mixtures of these substances. Susan Kaprov

This Chapter in Context

In Chapter 5 we discussed solutions as a medium for carrying out chemical reactions. Our focus at that time was on the kinds of reactions that take place in solution, and in particular, those that occur when water is the solvent. In this chapter we will examine how the addition of a solute affects the physical properties of the mixture. In our daily lives we take advantage of many of these effects. For example, we add ethylene glycol (antifreeze) to the water in a car's radiator to protect it against freezing and overheating because water has a lower freezing point and higher boiling point when solutes are dissolved in it.

Here we will study not only aqueous solutions, but also solutions involving other solvents. We will concentrate on liquid solutions, although solutions can also be gaseous or solid. In fact, all gases mix completely at the molecular level, so the gas mixtures we examined in Chapter 11 were gaseous solutions. Solid solutions, called alloys, include such materials as brass and bronze. Other solid solutions include paraffin wax which is a mixture of long-chain hydrocarbons, and gemstones such as ruby, garnet, and jade, which are solid solutions where metal ions contribute to their distinctive colors.

Gemstones are examples of solid solutions

Gem Name	Mineral	Colorant Atom(s)
Ruby	Al_2O_3	Cr, Fe
Sapphire	Al_2O_3	Cr, Ti, Fe
Turquoise	$CuAl_6(PO_4)_4(OH)_8 \cdot 5H_2O$	Cu
Emerald	$Be_3Al_2Si_6O_{18}$	Cr, V
Lapis lazuli	$(Na, Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2.$	S
Jade	$NaAlSi_2O_6$	Cr
Amethyst	SiO_2	Mn
Tanzanite	$Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$	Cr
Malachite	$Cu_2CO_3(OH)_2$	Cu

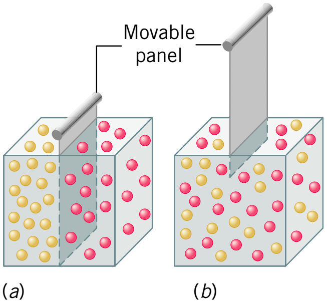
13.1 | Intermolecular Forces and the Formation of Solutions

There is a wide variation in the ability of liquids to dissolve solutes. For example, water and gasoline do not dissolve in each other, but water and ethanol can be mixed in all proportions. Similarly, a salt such as potassium bromide will dissolve in water but not in liquid hydrocarbons such as paint thinner. To understand the reasons for these differences, we must examine the factors that drive solution formation as well as those that inhibit it.

Gas Molecules and Spontaneous Mixing

In Chapter 11 you learned that all gases mix spontaneously to form homogeneous mixtures (i.e., solutions). If two gases are placed in separate compartments of a container such as that in Figure 13.1, and the movable partition between them is removed, the molecules will begin to intermingle. The random motions of the molecules will cause them to diffuse one into the other until a uniform mixture is achieved.

The spontaneous mixing of gases illustrates one of nature's strong "driving forces" for change. *A system, left to itself, will tend toward the most probable state.*[1] At the instant we remove the partition, the container holds two separate gas samples, in contact but unmixed. This represents a highly improbable state because of the natural motions of the molecules. The vastly more probable distribution is one in which the molecules are thoroughly mixed, so formation of the gaseous solution involves a transition from a highly improbable state to a highly probable one.



(*a*) (*b*)

Figure 13.1 | **Mixing of gases.** When two gases, initially in separate compartments (*a*), suddenly find themselves in the same container (*b*), they mix spontaneously.

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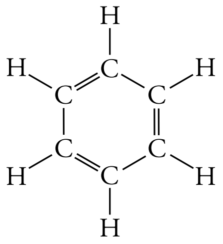
[1] In Chapter 19 this driving force will be called *entropy*.

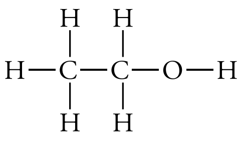
The drive to attain the most probable state favors the formation of *any* solution. What limits the ability of most substances to mix completely, however, are intermolecular forces of attraction. Such attractions are negligible in gases, so regardless of the chemical makeup of the molecules, the forces are unable to prevent them from mixing. That's why all gases spontaneously form solutions with each other. In liquids and solids, however, the situation is very different because intermolecular attractions are so much stronger.

Liquids Dissolving in Liquids

For a liquid solution to form, there must be a balance among the attractive forces so the natural tendency of particles to intermingle can proceed. In other words, the attractive forces between molecules within the solvent and between molecules within the solute must be about as strong as attractions between solute and solvent molecules. Let's look at two examples, mixtures of water with benzene and with ethanol.



benzene
(nonpolar)



ethanol
(contains a polar OH group)

Water and benzene (C_6H_6) are insoluble in each other. In water, there are strong hydrogen bonds between the molecules; in benzene the molecules attract each other by relatively weak London forces and are not able to form hydrogen bonds. Suppose that we did manage to disperse water molecules in benzene. As they move about, the water molecules would occasionally encounter each other. Because they attract each other so much more strongly than they attract benzene molecules, hydrogen bonds would cause water molecules to stick together at each such encounter. This would continue to happen until all the water was in a separate phase. Thus, a solution of water in benzene would not be stable and would gradually separate into two phases. We say water and benzene are **immiscible,** meaning they are mutually insoluble.

Water and ethanol (C_2H_5OH), on the other hand, are **miscible,** meaning that they are soluble in all proportions. This is because water and ethanol molecules can form hydrogen bonds with each other in mixtures that are nearly equivalent to those in the separate pure liquids (Figure 13.2). Mixing these molecules offers little resistance, so they are able to mingle relatively freely.

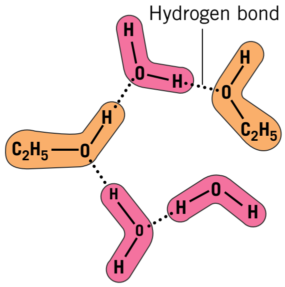


Figure 13.2 | **Hydrogen bonds in aqueous ethanol.** Ethanol molecules form hydrogen bonds (···) to water molecules.

Like Dissolves Like Rule

Observations like those for benzene–water and ethanol–water mixtures led to a generalization often called the **"like dissolves like" rule:** when solute and solvent have molecules "like" each other in polarity, they tend to form a solution. When solute and solvent molecules are quite different in polarity, solutions of any appreciable concentration do not form. The rule has long enabled chemists to use chemical composition and molecular structure to predict the likelihood of two substances dissolving in each other.

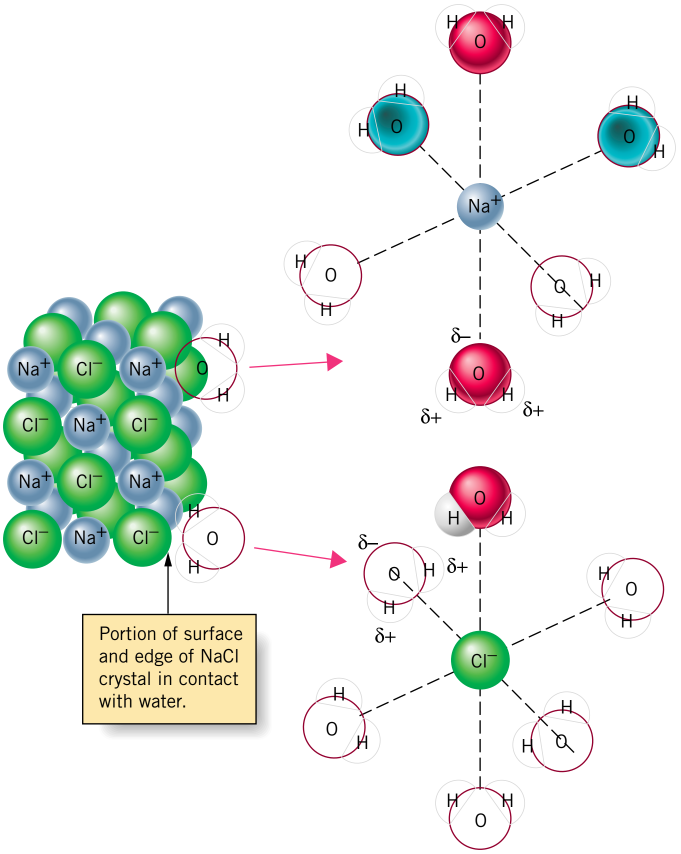
TOOLS

"Like dissolves like" rule

The Solubility of Solids in Liquids

The "like dissolves like" principle also applies to the solubility of solids in liquid solvents. Polar solvents tend to dissolve polar and ionic compounds, whereas nonpolar solvents tend to dissolve nonpolar compounds.

Figure 13.3 | **Hydration of ions.** Hydration involves a complex redirection of forces of attraction and repulsion. Before this solution forms, water molecules are attracted only to each other, and Na^+ and Cl^- ions have only each other to be attracted to in the crystal. In the solution, the ions have water molecules to take the places of their oppositely charged counterparts; in addition, water molecules are attracted to ions even more than they are to other water molecules.

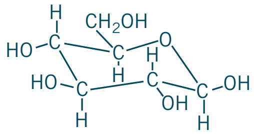


Portion of surface and edge of NaCl crystal in contact with water.

- Water molecules collide everywhere along the crystal surface, but *successful* collisions—those that dislodge ions—are more likely to occur at corners and edges.

Figure 13.3 depicts a section of a crystal of NaCl in contact with water. The dipoles of water molecules orient themselves so that the negative ends of some point toward Na^+ ions and the positive ends of others point at Cl^- ions. In other words, *ion–dipole* attractions occur that tend to tug and pull ions from the crystal. At the corners and edges of the crystal, ions are held by fewer neighbors within the solid and so are more readily dislodged than those elsewhere on the crystal's surface. As water molecules dislodge these ions, new corners and edges are exposed, and the crystal continues to dissolve.

As they become free, the ions become completely surrounded by water molecules (also shown in Figure 13.3). The phenomenon is called the **hydration** of ions. The *general* term for the surrounding of a solute particle by solvent molecules is **solvation,** so hydration is just a special case of solvation. Ionic compounds are able to dissolve in water when the attractions between water dipoles and ions overcome the attractions of the ions for each other within the crystal.



Sugar molecules such as this have polar OH groups that can form hydrogen bonds with water.

Similar events explain why solids composed of polar molecules, like those of sugar, dissolve in water (see Figure 13.4). Attractions between the solvent and solute dipoles help to dislodge molecules from the crystal and bring them into solution. Again we see that "like dissolves like," because a polar solute dissolves in a polar solvent.

The same reasoning explains why nonpolar solids like wax are soluble in nonpolar solvents such as benzene. Wax is a solid mixture of long-chain hydrocarbons, held together by London forces. The attractions between benzene molecules are also London forces, of comparable strength, so molecules of the wax can easily be dispersed among those of the solvent.

When intermolecular attractive forces within solute and solvent are sufficiently different, the two do not form a solution. For example, ionic solids or very polar molecular solids (like sugar) have strong attractions between their particles that cannot be overcome by attractions to molecules of a nonpolar solvent such as benzene.

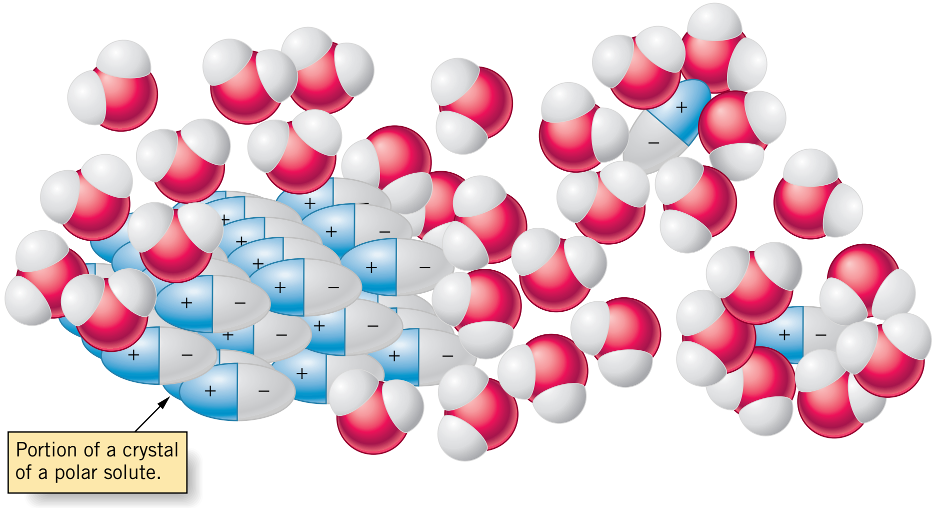

Portion of a crystal of a polar solute.
+
–

Figure 13.4 | Hydration of a polar molecule. A polar molecule of a molecular compound (such as the sugar glucose) can trade the forces of attraction it experiences for other molecules of its own kind for forces of attraction to molecules of water in an aqueous solution.

13.2 | Heats of Solution

Because intermolecular attractive forces are important when liquids and solids are involved, the formation of a solution is inevitably associated with energy exchanges. The total energy absorbed or released when a solute dissolves in a solvent at constant pressure to make a solution is called the *molar enthalpy of solution*,[2] or usually just the **heat of solution, ΔH_{soln}**.

Energy is required to separate the particles of solute and also those of the solvent and make them spread out to make room for each other. This step is *endothermic*, because we must overcome the attractions between molecules to spread the particles out. However, once the particles come back together as a *solution*, energy is released as the attractive forces between approaching solute and solvent particles decrease the system's potential energy. This is an *exothermic* change. The enthalpy of solution, ΔH_{soln}, is simply the net result of these two opposing enthalpy contributions.

Solutions of Solids in Liquids

Because enthalpy, H, is a state function, the magnitude of ΔH_{soln} doesn't depend on the path we take from the separated solute and solvent to the solution. For a solid dissolving in a liquid, it is convenient to imagine a two-step path.

Step 1. *Vaporize the solid to form individual solute particles.* The particles are molecules for molecular substances and ions for ionic compounds. The energy absorbed is equal in magnitude to, but with the opposite sign, as the lattice energy of the solid.

Step 2. *Bring the separated gaseous solute particles into the solvent to form the solution.* This step is exothermic, and the enthalpy change when the particles from one mole of solute are dissolved in the solvent is called the **solvation energy**. If the solvent is water, the solvation energy can also be called the **hydration energy**.

The enthalpy diagram showing these steps for potassium iodide is given in Figure 13.5. Step 1 corresponds to the negative of the lattice energy of KI, which is represented by the thermochemical equation.

$$\mathrm{KI}(s) \longrightarrow \mathrm{K}^+(g) + \mathrm{I}^-(g) \qquad \Delta H = +632 \text{ kJ}$$

---

[2] As a solute is dissolved, the properties of the solvent change because of the presence of previously dissolved solute. Therefore, even if we know the molar heat of solution, we cannot precisely calculate the heat evolved when more, or less, than one mole of solute is dissolved in a liter of solvent.

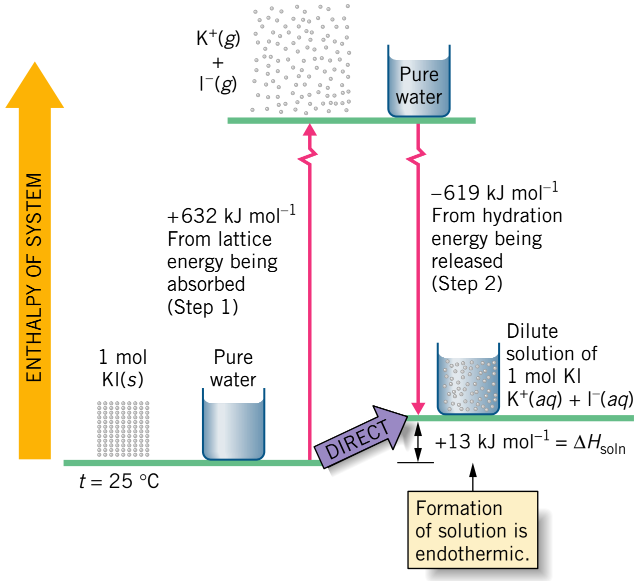

$K^+(g)$
+
$I^-(g)$
Pure water
$+632$ kJ mol^{-1}
From lattice energy being absorbed
(Step 1)
-619 kJ mol^{-1}
From hydration energy being released
(Step 2)
ENTHALPY OF SYSTEM
1 mol KI(s)
Pure water
Dilute solution of 1 mol KI
$K^+(aq) + I^-(aq)$
DIRECT
$+13$ kJ mol^{-1} = ΔH_{soln}
t = 25 °C
Formation of solution is endothermic.

Figure 13.5 | **Enthalpy diagram for the heat of solution of one mole of potassium iodide.** Adding the negative of the lattice energy to the hydration energy gives a positive value for ΔH_{soln}, indicating the solution process is endothermic.

Step 2 corresponds to the hydration energy of gaseous K^+ and I^- ions.

$$K^+(g) + I^-(g) \longrightarrow K^+(aq) + I^-(aq) \qquad \Delta H = -619 \text{ kJ}$$

The *enthalpy of solution* is obtained from the sum of the equations for Steps 1 and 2 and is the enthalpy change when one mole of crystalline KI dissolves in water (corresponding to the direct path in Figure 13.5).

$$KI(s) \longrightarrow K^+(aq) + I^-(aq) \qquad \Delta H_{soln} = +13 \text{ kJ}$$

The value of ΔH_{soln} indicates that the solution process is endothermic for KI, in agreement with the observation that when KI is added to water and the mixture is stirred, it becomes cool as the KI dissolves.

Table 13.1 provides a comparison between values of ΔH_{soln} obtained by the method described above and values obtained by direct measurements. The agreement between calculated and measured values doesn't seem particularly impressive, but this is partly because lattice and hydration energies are not precisely known and partly because the model used in our analysis is evidently too simple. Notice, however, that when "theory" predicts relatively large heats of solution, the experimental values are also relatively large, and that both values have the same sign (except for NaBr). Notice also that the variations among the values follow the same trends when we compare the three chloride salts—LiCl, NaCl, and KCl—or the three bromide salts—LiBr, NaBr, and KBr.

■ Small percentage errors in very large numbers can cause huge uncertainties in the *differences* between such numbers.

Solutions of Liquids in Liquids

To consider heats of solution when liquids dissolve in liquids, it's useful to imagine a three-step path going from the initial to the final state (see Figure 13.6). We will designate one liquid as the solute and the other as the solvent.

Step 1. *Expand the solute liquid.* First, we imagine that the molecules of one liquid are moved apart just far enough to make room for molecules of the other liquid. Because we have to overcome forces of attraction, this step increases the system's potential energy and so is *endothermic*.

Table 13.1 **Lattice Energies, Hydration Energies, and Heats of Solution for Some Group 1A Metal Halides**

			ΔH_{soln}[a]	
Compound	**Lattice Energy (kJ mol^{-1})**	**Hydration Energy (kJ mol^{-1})**	**Calculated[b] ΔH_{soln} (kJ mol^{-1})**	**Measured ΔH_{soln} (kJ mol^{-1})**
LiCl	−853	−883	−30	−37.0
NaCl	−786	−770	+16	+3.9
KCl	−715	−686	+29	+17.2
LiBr	−807	−854	−47	−49.0
NaBr	−747	−741	+6	−0.602
KBr	−682	−657	+25	+19.9
KI	−649	−619	+30	+20.33

[a] Heats of solution refer to the formation of extremely dilute solutions.

[b] Calculated ΔH_{soln} = hydration energy − lattice energy.

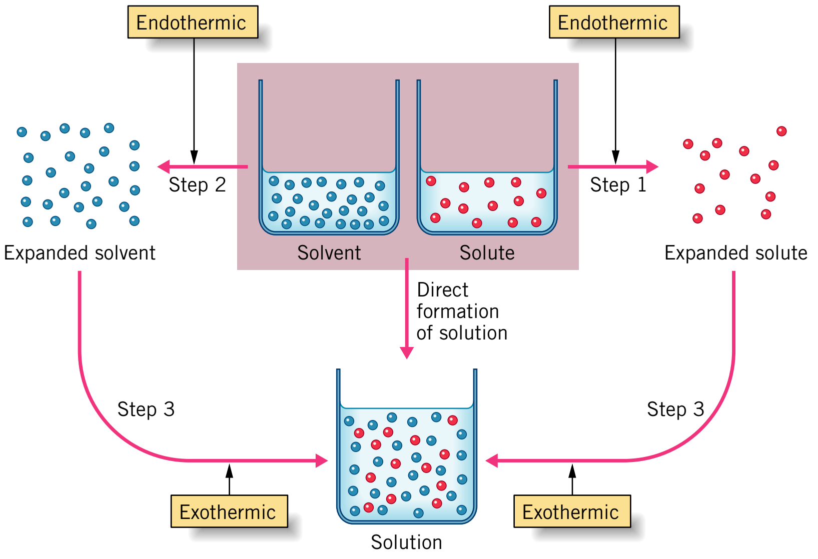

Endothermic
Endothermic
Step 2
Step 1
Expanded solvent
Solvent
Solute
Expanded solute
Direct formation of solution
Step 3
Step 3
Exothermic
Exothermic
Solution

Figure 13.6 | **Enthalpy of solution for the mixing of two liquids.** To analyze the enthalpy change for the formation of a solution of two liquids, we can imagine the hypothetical steps shown here. **Step 1:** The molecules of the liquid designated as the solvent move apart slightly to make room for the solute molecules, an endothermic process. **Step 2:** The molecules of the solute are made to take up a larger volume to make room for the solvent molecules, which is also an endothermic change. **Step 3:** The expanded samples of solute and solvent spontaneously intermingle, their molecules also attracting each other, making the step exothermic.

Step 2. *Expand the solvent liquid.* The second step is like the first, but is done to the other liquid (the solvent). On an enthalpy diagram (Figure 13.7) we have climbed two energy steps and have both the solvent and the solute in their slightly "expanded" conditions.

Step 3. *Mix the expanded liquids.* The third step brings the molecules of the expanded solvent and solute together to form the solution. Because the molecules of the two liquids experience mutual forces of attraction, bringing them together lowers the system's potential energy, so Step 3 is exothermic. The value of ΔH_{soln} will, again, be the net energy change for these steps.

Ideal Solutions

The enthalpy diagram in Figure 13.7 shows the special case when the sum of the energy inputs for Steps 1 and 2 is equal to the energy released in Step 3, so the overall value of ΔH_{soln} is zero. This is very nearly the case when we make a solution of benzene and carbon tetrachloride. Attractive forces between molecules of benzene are almost exactly the same as those between molecules of CCl_4, or between molecules of benzene and those of CCl_4. If all such intermolecular forces were identical, the net ΔH_{soln} would be exactly zero, and the resulting solution would be called an **ideal solution**. Be sure to notice the difference between an *ideal solution* and an *ideal gas*. In an ideal gas, there are *no* attractive forces. In an ideal solution, there are attractive forces, but they are all the *same*.

For most liquids that are mutually soluble, ΔH_{soln} is not zero. Instead, heat is either given off or absorbed. For example, acetone and water are liquids that form a solution exothermically (ΔH_{soln} is negative.). With these liquids, the third step releases more energy

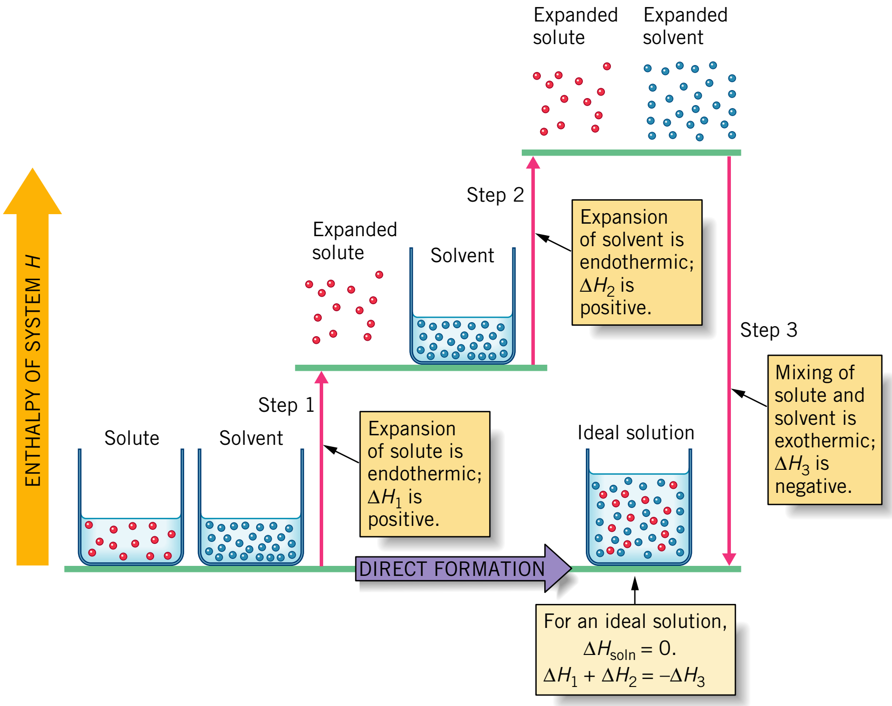
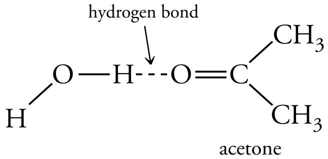

Expanded solute
Expanded solvent
Step 2
Expansion of solvent is endothermic; ΔH_2 is positive.
Expanded solute
Solvent
ENTHALPY OF SYSTEM H
Step 3
Step 1
Solute
Solvent
Expansion of solute is endothermic; ΔH_1 is positive.
Ideal solution
Mixing of solute and solvent is exothermic; ΔH_3 is negative.
DIRECT FORMATION
For an ideal solution, $\Delta H_{\text{soln}} = 0.$ $\Delta H_1 + \Delta H_2 = -\Delta H_3$

Figure 13.7 | **Enthalpy changes in the formation of an ideal solution.** The three-step and the direct-formation paths both start and end at the same place with the same enthalpy outcome. The sum of the positive ΔH values for the two endothermic steps, 1 and 2, numerically equals the negative ΔH value for the exothermic step, 3. The net ΔH for the formation of an ideal solution is therefore zero.

than the sum of the first two, chiefly because molecules of water and acetone attract each other more strongly than acetone molecules attract each other. This is because water molecules can form hydrogen bonds to acetone molecules in the solution, but acetone molecules cannot form hydrogen bonds to other acetone molecules in the pure liquid.


hydrogen bond
acetone

Another pair of liquids, ethanol and hexane form a solution endothermically. In this case, the release of energy in the third step is not enough to compensate for the energy demands of Steps 1 and 2, so the solution cools as it forms. Since hydrogen-bonded ethanol molecules attract each other more strongly than they can attract hexane molecules, hexane molecules cannot push their way into ethanol without added energy to disrupt some of the hydrogen bonding between ethanol molecules.

■ $CH_3CH_2CH_2CH_2CH_2CH_3$
hexane

Gas Solubility

Unlike solid and liquid solutes, only very weak attractions exist between gas molecules, so the energy required to "expand the solute" is negligible. The heat absorbed or released when a gas dissolves in a liquid has essentially two contributions, as shown in Figure 13.8:

1. *Energy is absorbed when "pockets" in the solvent are opened to hold gas molecules.* The solvent must be expanded slightly to accommodate the molecules of the gas. This requires a small energy input, since attractions between solvent molecules must be overcome. Water is a special case; it already contains open holes in its network of loose hydrogen bonds around room temperature. For water, very little energy is required to create pockets that can hold gas molecules.
2. *Energy is released when gas molecules occupy these pockets.* Intermolecular attractions between the gas molecules and the surrounding solvent molecules lower the total energy, and energy is released as heat. The stronger the attractions are, the more heat is released. Water is capable of forming hydrogen bonds with some gases, such as ammonia and hydrogen fluoride, while organic solvents often can't.

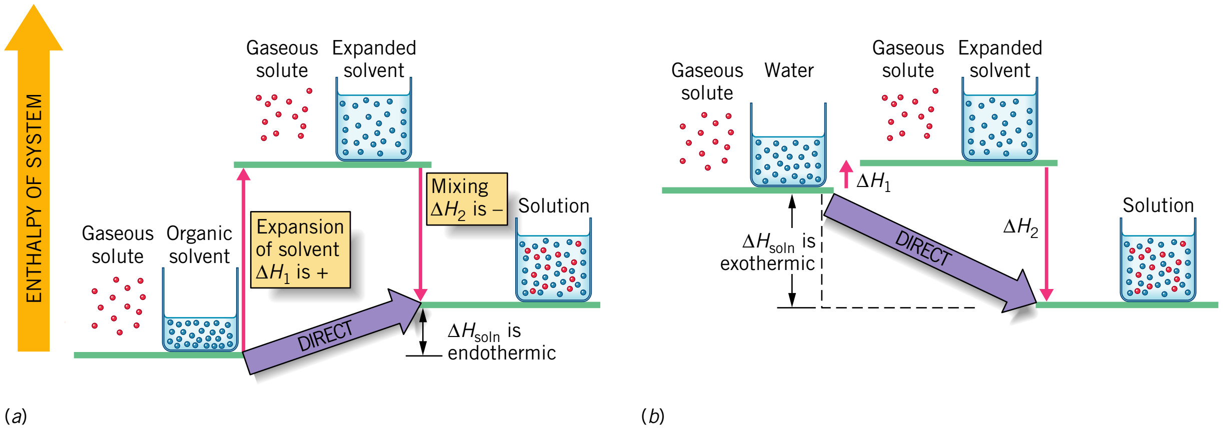

ENTHALPY OF SYSTEM
Gaseous solute
Organic solvent
Expansion of solvent ΔH_1 is +
Gaseous solute
Expanded solvent
Mixing ΔH_2 is –
Solution
DIRECT
ΔH_{soln} is endothermic
(a)
Gaseous solute
Water
ΔH_1
ΔH_{soln} is exothermic
Gaseous solute
Expanded solvent
DIRECT
ΔH_2
Solution
(b)

Figure 13.8 | **A molecular model of gas solubility.** (*a*) A gas dissolves in an organic solvent. Energy is absorbed to open "pockets" in the solvent that can hold the gas molecules. In the second step, energy is released when the gas molecules enter the pockets, where they are attracted to the solvent molecules. Here the solution process is shown to be endothermic. (*b*) At room temperature, water's loose network of hydrogen bonds already contains pockets that can accommodate gas molecules, so little energy is needed to prepare the solvent to accept the gas. In the second step, energy is released as the gas molecules take their places in the pockets, where they experience attractions to the water molecules. In this case, the solution process is exothermic.

A larger amount of heat is released when a gas molecule is placed in the pocket in water than when it is placed in organic solvents.

These factors lead to two generalizations. *First, heats of solution for gases in organic solvents are often endothermic* because the energy required to open up pockets is greater than the energy released by attractions formed between the gas and solvent molecules. *Second, heats of solution for gases in water are often exothermic* because water already contains pockets to hold the gas molecules, and energy is released when water and gas molecules attract each other.

13.3 | Solubility as a Function of Temperature

By "solubility" we mean the mass of solute that forms a *saturated* solution with a given mass of solvent at a specified temperature. The units often are grams of solute per 100 g of solvent. In such a solution there is a dynamic equilibrium between the undissolved solute and the solute dissolved in the solution, as shown in the equation below and in Figure 13.9.

$$\underset{\text{(Solute contacts the saturated solution.)}}{\text{solute}_{\text{undissolved}}} \rightleftharpoons \underset{\text{(Solute is in the saturated solution.)}}{\text{solute}_{\text{dissolved}}}$$

As long as the temperature is held constant, the concentration of the solute in the solution remains the same. However, if the temperature of the mixture changes, this equilibrium tends to be upset and either more solute will dissolve or some will precipitate. To analyze how temperature affects solubility we can use Le Châtelier's principle, which we introduced in Chapter 12. Recall that this principle tells us that if a system at equilibrium is disturbed, the system will change in a direction that counteracts the disturbance and returns the system to equilibrium (if it can).

To increase the temperature of a solution, heat (energy) is added. When solute dissolves in a solvent, heat is absorbed or evolved. As in Section 12.9, heat is the factor through which Le Châtelier's principle is applied. Let's consider a common situation in which energy is absorbed when the last few solute molecules are dissolved in preparing a saturated solution.[3]

$$\text{solute}_{\text{undissolved}} + \text{energy} \rightleftharpoons \text{solute}_{\text{dissolved}} \tag{13.1}$$

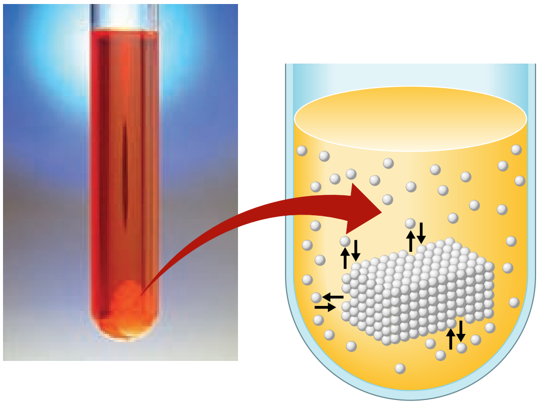


Figure 13.9 | **Molecular view of a saturated solution.** A saturated solution involves a dynamic equilibrium between the solid crystal and the dissolved particles. The arrows indicate that dissolving is occurring as rapidly as crystallization. *(Charles D. Winters/PhotoResearchers)*

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[3] The heat of solution depends on the solute and the solvent. When preparing a solution, the added solute can be considered to be unchanging as it is added to the solution; however, the solvent does change. At the start, we add solute to pure solvent. Later in the process, we are adding solute to a mixture of solvent and solute. The solution process is one where solute is added to a continuously changing solvent. We find that the incremental heat of solution (i.e., heat evolved per gram of solute added) changes as the solvent changes and can even change from exothermic to endothermic. Interestingly, the incremental heats of solution of solutes added to a nearly saturated solution are almost all endothermic.

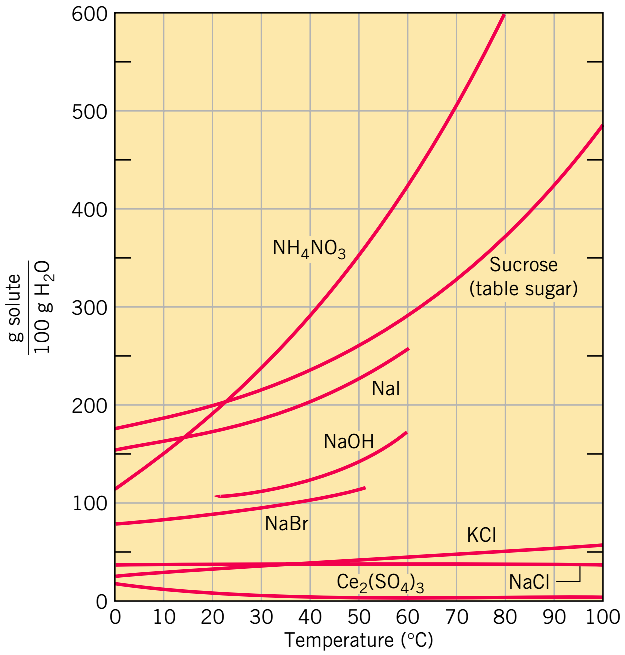

Figure 13.10 | **Solubility in water versus temperature for several substances.** Most substances become more soluble when the temperature of the solution is increased, but the amount of this increased solubility varies considerably.

According to Le Châtelier's principle, when we add heat energy to raise the temperature, the system responds by consuming some of the energy we've added. This causes the equilibrium in Equation 13.1 to "shift to the right." In other words, more solute is dissolved when equilibrium is reestablished. Thus, *when the solution process is endothermic (and it usually is endothermic near the saturation point), raising the temperature will increase the solubility of the solute.* This is a common situation for solids dissolving in liquid solvents. How much the solubility is affected by temperature varies widely, as seen in Figure 13.10.

Some solutes, such as cerium(III) sulfate, $Ce_2(SO_4)_3$, become *less* soluble with increasing temperature (Figure 13.10). Energy must be *released* from a saturated solution of $Ce_2(SO_4)_3$ to make more solute dissolve. For its equilibrium equation, we must show "energy" on the right side because heat is released.

$$\text{solute}_{\text{undissolved}} \rightleftharpoons \text{solute}_{\text{dissolved}} + \text{energy} \qquad (13.2)$$

Raising the temperature by adding heat causes dissolved solute to precipitate.

Temperature and Gas Solubility

Table 13.2 lists the solubilities of several common gases in water at different temperatures, but all under 1 atm of pressure. In water, gases such as oxygen are usually more soluble at colder temperatures. Dissolved oxygen in lakes, streams, and oceans is extracted through the gills of marine animals. Fish generally seek colder waters because of the higher concentration of oxygen. **Hypoxia,** a condition in which oxygen concentrations are critically low, has been known to cause massive fish kills.

The solubility of gases, like other solubilities, can increase or decrease with temperature, depending on the gas and the solvent. For example, the solubilities of H_2, N_2, CO, He, and Ne actually increase with rising temperature in common organic solvents like carbon tetrachloride, toluene, and acetone.

Table 13.2 Solubilities of Common Gases in Water[a]

	Temperature			
Gas	**0 °C**	**20 °C**	**50 °C**	**100 °C**
Nitrogen, N_2	0.0029	0.0019	0.0012	0
Oxygen, O_2	0.0069	0.0043	0.0027	0
Carbon dioxide, CO_2	0.335	0.169	0.076	0
Sulfur dioxide, SO_2	22.8	10.6	4.3	1.8[b]
Ammonia, NH_3	89.9	51.8	28.4	7.4[c]

[a] Solubilities are in grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 1 atm.

[b] Solubility at 90 °C.

[c] Solubility at 96 °C.

13.4 | Henry's Law

The solubility of a gas in a liquid increases with increasing pressure. To understand this at the molecular level, imagine the following equilibrium established in a closed container fitted with a movable piston (Figure 13.11*a*).

$$\text{gas} + \text{solvent} \rightleftharpoons \text{solution} \qquad \textbf{(13.3)}$$

If the piston is pushed down (Figure 13.11*b*), the gas is compressed and its pressure increases. This causes the concentration of the gas molecules over the solution to increase, so the rate at which the gas dissolves is now greater than the rate at which it leaves the solution. Eventually, equilibrium is reestablished when the concentration of the gas in the solution has increased enough to make the rate of escape equal to the rate at which the gas dissolves (Figure 13.11*c*). At this point, the concentration of the gas in the solution is higher than before.

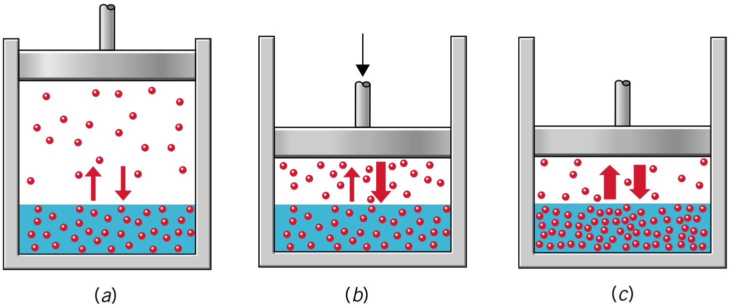
(*a*) (*b*) (*c*)

Figure 13.11 | **How pressure increases the solubility of a gas in a liquid.** (*a*) At some specific pressure, equilibrium exists between the vapor phase and the solution. (*b*) An increase in pressure upsets the equilibrium. More gas molecules are dissolving than are leaving the solution. (*c*) More gas has dissolved and equilibrium is restored.

The effect of pressure on the solubility of a gas can also be explained by Le Châtelier's principle and Equation 13.3. In this case, the disturbance is an increase in the pressure of the gas above the solution. How could the system counteract the pressure increase? The answer is: by having more gas dissolve in the solution. In this way, the pressure of the gas is reduced and the concentration of the gas in the solution is increased. In other words, increasing the pressure of the gas will cause the gas to become more soluble.

Figure 13.12 shows how the solubility in water of oxygen and nitrogen vary with pressure. The straight lines on the graph indicate that the concentration of the gas is directly proportional to its pressure above the solution. This is expressed quantitatively by **Henry's law**, which states that *the concentration of a gas in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution.*

■ William Henry (1774–1836), an English chemist, first reported the relationship between gas solubility and pressure.

$$C_{\text{gas}} = k_{\text{H}} P_{\text{gas}} \qquad (T \text{ is constant}) \qquad \textbf{(13.4)}$$

TOOLS

Henry's law

where C_{gas} is the concentration of the gas and P_{gas} is the partial pressure of the gas above the solution. The proportionality constant, k_{H}, called the Henry's law constant, is unique to each gas. The equation is an approximation that works best at low concentrations and pressures and for gases that do not react with the solvent.

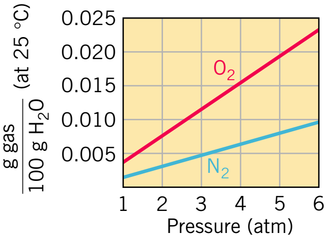

Figure 13.12 | **Solubility in water versus pressure for two gases**. The amount of gas that dissolves increases as the pressure is raised.

Bottled carbonated beverages fizz when the bottle is opened because the sudden drop in pressure causes a sudden drop in gas solubility. *(Andy Washnik)*

An alternate (and commonly used) form of Henry's law is

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \tag{13.5}$$

where the subscripts 1 and 2 refer to initial and final conditions, respectively. By taking the ratio, the Henry's law constant cancels.

Example 13.1
Solubility of Nitrogen Using Henry's Law

At 20.0 °C the solubility of N_2 in water is 0.0152 g L^{-1} when the partial pressure of nitrogen is 585 torr. What will be the solubility of N_2 in water at 20.0 °C when its partial pressure is 823 torr?

Analysis: This problem deals with the effect of gas pressure on gas solubility, so Henry's law applies.

Assembling the Tools: We use Henry's law in its form given by Equation 13.5 because it lets us avoid having to know or calculate the Henry's law constant.

Solution: Let's gather the data first, making sure to distinguish between the initial (C_1 and P_1) and final conditions (C_2 and P_2).

$$C_1 = 0.0152\ \text{g L}^{-1} \qquad C_2 = \text{unknown}$$
$$P_1 = 585\ \text{torr} \qquad P_2 = 823\ \text{torr}$$

Using Equation 13.5, we have

$$\frac{0.0152\ \text{g L}^{-1}}{585\ \text{torr}} = \frac{C_2}{823\ \text{torr}}$$

After multiplying both sides by 823 torr we solve for C_2,

$$C_2 = 0.0214\ \text{g L}^{-1}$$

The solubility under the higher pressure is 0.0214 g L^{-1}.

Is the Answer Reasonable? In relationship to the initial concentration, the size of the answer makes sense because Henry's law tells us to expect a greater solubility at the higher pressure.

Practice Exercises

13.1 | At 25 °C and standard pressure, a hydrogen sulfide solution can be made by bubbling $H_2S(g)$ into water; the result is a 0.11 molar solution. Since $H_2S(g)$ is more dense than air we can assume that a layer of pure $H_2S(g)$ at atmospheric pressure covers the solution. What is the value of Henry's law constant, and is the solubility of $H_2S(g)$ much greater or smaller than other gases mentioned in this section? If so, suggest a reason for the difference. (*Hint:* What is the pressure of the $H_2S(g)$?)

13.2 | How many grams of nitrogen and oxygen are dissolved in 125 g of water at 20.0 °C when the water is saturated with air? At 1.00 atm pressure, the solubility of pure oxygen in water is 0.00430 g O_2/100.0 g H_2O, and the solubility of pure nitrogen in water is 0.00190 g N_2/100.0 g H_2O. In pure, dry air, P_{N_2} equals 593 torr and P_{O_2} equals 159 torr.

Solutions of Gases that React with Water

The gases sulfur dioxide, ammonia, and, to a lesser extent, carbon dioxide are far more soluble in water than are oxygen or nitrogen (see Table 13.2). Part of the reason is that SO_2, NH_3, and CO_2 molecules have polar bonds and sites of partial charge that attract water molecules, forming hydrogen bonds to help hold the gases in solution. Ammonia molecules, in addition, not only can accept hydrogen bonds from water ($\text{O—H}\cdots\text{N}$) but also can donate them through their N—H bonds ($\text{N—H}\cdots\text{O}$).

The more soluble gases, dissolved, also react with water to some extent as the following chemical equilibria show.

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HCO_3^-}(aq)$$
$$\mathrm{SO_2}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HSO_3^-}(aq)$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

The forward reactions contribute to the higher concentrations of the gases in solution, as compared to gases such as O_2 and N_2 that do not react with water at all. Gaseous sulfur trioxide is very soluble in water because it reacts *quantitatively* (i.e., completely) with water to form sulfuric acid.[4]

$$\mathrm{SO_3}(g) + \mathrm{H_2O} \longrightarrow \mathrm{H^+} + \mathrm{HSO_4^-}(aq)$$

13.5 | Temperature-Independent Concentration Units

In Section 5.6 you learned that for stoichiometry, *molar concentration* or *molarity,* mol/L, is a convenient unit of concentration because it lets us measure out moles of a solute simply by measuring volumes of solution. For studying physical and chemical properties, at different temperatures, molarity is not preferred because the molarity of a solution varies slightly with temperature. Most liquids expand slightly when heated, so a given solution will have a larger volume, and therefore a lower ratio of moles to volume, as its temperature is raised. When our measurements must be made at several different temperatures, temperature-independent concentration units are used. The most common of these are *percentage by mass*, *molality*, and *mole fraction* (or *mole percent*).

Percent Concentration

Concentrations of solutions are often expressed as a **percentage by mass** (sometimes called a *percent by weight*), which gives grams of solute per 100 grams of solution. Percentage by mass is indicated by % (w/w), where the "w" stands for "weight." To calculate a percentage by mass from solute and solution masses, we can use the **mass fraction** (the mass of solute divided by the mass of the solution) and multiply it by 100% as shown in the following formula:

$$\text{Percentage by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \qquad (13.6)$$

TOOLS

Percentage by mass

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[4] The "concentrated sulfuric acid" of commerce has a concentration of 93 to 98% H_2SO_4, or roughly 18 *M*. This solution takes up water avidly and very exothermically, removing moisture even out of humid air itself (and so must be kept in stoppered bottles). Because it is dense, oily, sticky, and highly corrosive, it must be handled with extreme care. Safety goggles and gloves must be worn when dispensing concentrated sulfuric acid. When making a more dilute solution, *always pour (slowly with stirring) the concentrated acid into the water.* If water is poured onto concentrated sulfuric acid, it can layer on the acid's surface, because the density of the acid is so much higher than water's (1.8 g mL^{-1} vs. 1.0 g mL^{-1} for water). At the interface, such intense heat can be generated that the steam thereby created could explode from the container, spattering acid around.

For example, a solution labeled "0.85% (w/w) NaCl" is one in which the ratio of solute to solution is 0.85 g of NaCl to 100.00 g of NaCl solution. This suggests that the percent concentration can be used as a conversion factor as illustrated in the following example. Also illustrated in this example is that often, the "(w/w)" symbol is omitted when writing mass percents.[5]

Percentages could also be called *parts per hundred*. Other similar expressions of concentration are *parts per million* (ppm) and *parts per billion* (ppb), where 1 ppm equals 1 g of component in 10^6 g of the mixture and 1 ppb equals 1 g of component in 10^9 g of the mixture. By analogy, we can see that ppm is simply the mass fraction multiplied by 10^6 ppm and ppb is the mass fraction multiplied by 10^9 ppb.

Example 13.2
Using Percent Concentrations

Seawater is typically 3.5% sea salt and has a density of 1.03 g mL^{-1}. How many grams of sea salt would be needed to prepare enough seawater solution to completely fill a 62.5 L aquarium?

■ **Analysis:** We need the number of grams of sea salt in 62.5 L of seawater solution. To solve the problem, we'll need a relationship that links seawater and sea salt. The percent concentration in Equation 13.6 is the link we need. We will assume that the percent is a percentage by mass.

■ **Assembling the Tools:** We can write "3.5% sea salt" as the following conversion equality:

$$3.5 \text{ g sea salt} \Leftrightarrow 100 \text{ g soln}$$

Density (see Section 2.5 page 51) provides the next conversion equality,

$$1.03 \text{ g soln} \Leftrightarrow 1.00 \text{ mL soln}$$

Finally, we will use the SI prefixes in Table 2.4, page 35 to convert mL to liters.

■ **Solution:** We will start by writing the question in equation form:

$$62.5 \text{ L soln} \Leftrightarrow ?\ \text{g sea salt}$$

The hard work has been done. We just need to assemble the information in a logical sequence and cancel the units.

$$62.5\ \cancel{\text{L soln}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\ \cancel{\text{L soln}}} \times \frac{1.03\ \cancel{\text{g soln}}}{1\ \cancel{\text{mL soln}}} \times \frac{3.5\ \text{g sea salt}}{100\ \cancel{\text{g soln}}} = 2.3 \times 10^3\ \text{g sea salt}$$

■ **Is the Answer Reasonable?** If seawater is about 4% sea salt, 100 g of seawater should contain about 4 g of salt. A liter of seawater weighs about 1000 g, so it would contain about 40 g of salt. We have about 60 L of seawater, which would contain 60 × 40 g of salt, or 2400 g of salt. This is not too far from our answer, so the answer seems reasonable.

---

[5] Clinical laboratories sometimes report concentrations as **percent by mass/volume**, using the symbol "%(w/v)":

$$\text{percent by mass/volume} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$

For example, a solution that is 4%(w/v) $SrCl_2$ contains 4 g of $SrCl_2$ dissolved in 100 mL of solution. Notice that with a percent by mass, we can use any units for the mass of the solute and mass of the solution, as long as they are the same for both. With percent by mass/volume, we *must* use grams for the mass of solute and milliliters for the volume of solution. If a percent concentration does not include a (w/v) or (w/w) designation, we assume that it is a percentage by mass.

Practice Exercises

13.3 | What volume of water at 20.0 °C ($d = 0.9982\ \mathrm{g\ cm^{-3}}$) is needed to dissolve 45.0 g of sucrose to make a 10.0 %(w/w) solution? (*Hint:* You need the mass of water to solve this problem.)

13.4 | How many grams of NaBr are needed to prepare 25.0 g of 1.00%(w/w) NaBr solution in water? How many grams of water are needed? How many milliliters are needed, given that the density of water at room temperature is $0.988\ \mathrm{g\ mL^{-1}}$?

13.5 | Muriatic acid is the commercial name for hydrochloric acid that can be purchased from hardware stores as a solution that is 37%(w/w) HCl. What mass of this solution contains 7.5 g of HCl?

Molal Concentration

The number of moles of solute per kilogram of *solvent* is called the **molal concentration** or the **molality** of a solution. The usual symbol for molality is ***m***.

$$\text{Molality} = m = \frac{\text{mol of solute}}{\text{kg of solvent}} \tag{13.7}$$

Molal concentration

For example, if we dissolve 0.500 mol of sugar in 1.00 kg of water, we have a 0.500 *m* solution of sugar. We would not need a volumetric flask to prepare the solution, because we weigh the solvent. Some important physical properties of a solution are related in a simple way to its molality, as we'll soon see.

It is important not to confuse *molarity* with *molality*.

$$\text{Molality} = m = \frac{\text{mol of solute}}{\text{kg of } solvent} \qquad \text{Molarity} = M = \frac{\text{mol of solute}}{\text{L of } solution}$$

■ Be sure to notice that molality is defined per kilogram of *solvent*, not kilogram of solution.

As we pointed out at the beginning of this section, the molarity of a solution changes slightly with temperature, but molality does not. Therefore, molality is more convenient in experiments involving temperature changes. As we saw with molarity, molality can be used as a conversion factor. For example, the sugar solution above gives us the following equivalence:

$$0.500\ \text{mol sugar} \Leftrightarrow 1.00\ \text{kg}\ H_2O$$

When water is the solvent, a solution's molarity approaches its molality as the solution becomes more dilute. In very dilute solutions, 1.00 L of *solution* is nearly 1.00 L of pure water, which has a mass close to 1.00 kg. Under these conditions, the ratio of moles/liter (molarity) is very nearly the same as the ratio of moles/kilogram (molality).

■ This only applies when the solvent is water. For other solvents, molarity and molality have quite different values for the same solution.

Example 13.3
Preparation of a Solution of a Given Molality

An experiment calls for a 0.150 *m* solution of sodium chloride in water. How many grams of NaCl would have to be dissolved in 500.0 g of water to prepare a solution of this molality?

■ **Analysis:** In this problem, we are given two numerical values: the molality and the mass of water. Since we just saw that the molality can be used as a conversion factor, we will use to determine the mass of NaCl we need to dissolve in 500.0 g of water.

■ **Assembling the Tools:** First, we can use the given molality to write

$$0.150\ \text{mol NaCl} \Leftrightarrow 1.00\ \text{kg}\ H_2O$$

Next we need to determine the molar mass of NaCl (22.99 + 35.45 = 58.44 g NaCl mol^{-1}) to write the conversion equality between moles and mass,

$$1\ \text{mol NaCl} = 58.44\ \text{g NaCl}$$

Solution: We now write the question in equation form as

$$500.0\ \text{g H}_2\text{O} = ?\ \text{g NaCl}$$

and then we write the appropriate conversion factors as shown next.

$$500.0\ \cancel{\text{g H}_2\text{O}} \times \frac{0.150\ \cancel{\text{mol NaCl}}}{1.00 \times 10^3\ \cancel{\text{g H}_2\text{O}}} \times \frac{58.44\ \text{g NaCl}}{1\ \cancel{\text{mol NaCl}}} = 4.38\ \text{g NaCl}$$

When 4.38 g of NaCl is dissolved in 500.0 g of H_2O, the concentration is 0.150 *m* NaCl.

Is the Answer Reasonable? We'll round the formula mass of NaCl to 60, so 0.15 mol would weigh about 9 g. A 0.15 *m* solution would contain about 9 g NaCl in 1.00 kg of water. If we used only 500 g of water, we would need half as much salt, or about 4.5 g. Our answer is close to this, so it seems reasonable.

Practice Exercises

13.6 | If you prepare a solution by dissolving 44.00 g of sodium sulfate in 250.0 g of water, what is the molality of the solution? Is the molarity of this solution numerically larger or smaller than its molality? (*Hint:* Recall the definition of molality and molarity—see Sections 5.6 and 13.5 above.)

13.7 | Water freezes at a lower temperature when it contains solutes. To study the effect of methanol on the freezing point of water, we might begin by preparing a series of solutions of known molalities. Calculate the number of grams of methanol (CH_3OH) needed to prepare a series of solutions from 0.050 to 0.250 *m* in 0.050 *m* increments. For each solution use 200.0 g of water.

13.8 | What mass of a 0.853 molal solution of iron(III) nitrate is needed to obtain (a) 0.0200 moles of iron(III) nitrate, (b) 0.0500 moles of Fe^{3+} ions, (c) 0.00300 moles of nitrate ions?

Mole Fraction and Mole Percent

Mole fraction and mole percent are important tools that were discussed in Chapter 11 (page 502), so for the sake of completeness we will just review the definitions. The mole fraction, X_A, of a substance A is given by

$$X_A = \frac{n_A}{n_A + n_B + n_C + n_D + \cdots + n_Z} \tag{13.8}$$

where $n_A, n_B, n_C, \ldots, n_Z$ are the numbers of moles of each component, $A, B, C, \ldots, Z$ respectively. The sum of all mole fractions for a mixture must always equal 1. The **mole percent** is obtained by multiplying the mole fraction by 100 mol%.

$$\text{mol percent A} = \frac{n_A}{n_A + n_B + n_C + n_D + \cdots + n_Z} \times 100\ \text{mol\%} \tag{13.9}$$

The mole fractions of all components of a mixture add up to 1.00, so the mole percents must add up to 100 mol%.

Conversions among Concentration Units

There are times when we need to change from one concentration unit to another. The following example shows that, when converting from one temperature-independent concentration unit to another, all the information we need is in the definitions of the units. As you perform more complex conversions, it may be helpful to construct a table of data similar to the one below. Then you will have all the information needed at your fingertips.

Solvent	**Solute**	**Solution**
Mass	Mass	Total mass
Moles	Moles	Total moles
Volume	Volume	Total volume
Solvent molar mass	Solute molar mass	Density

Use a table such as this to keep track of solution data. Items in green are often found in tables if not given in a problem. Red items are replaced with known data. Perform conversions, as needed, to fill in remaining boxes.

Example 13.4

Finding Molality from Mass Percent

Brine is a fairly concentrated solution of sodium chloride in water. One use for brine is in the curing process for certain cheeses, where the concentration of brine affects the quality of the cheese. A supplier offers a cheese manufacturer a good price on 1.90 m brine. The cheesemaker needs a 10.0% (w/w) aqueous NaCl solution. Show whether or not the 1.90 m brine solution will be okay to use.

Analysis: In this problem we have a choice of methods to compare 1.90 m and 10.0% (w/w) brine to see whether they are equivalent. We can convert molality to %(w/w) or %(w/w) to molality. Let's do the latter conversion of %(w/w) to molality. First, we write the conversion we are asked to perform in equation form.

$$\frac{10.0\ \text{g NaCl}}{100.0\ \text{g NaCl soln}} \quad \text{to} \quad \frac{?\ \text{mol NaCl}}{1.00\ \text{kg water}}$$

This will involve conversion of mass to moles for NaCl and g to kg for water.

Assembling the Tools: The equality for converting mass to moles is

$$58.44\ \text{g NaCl} = 1.00\ \text{mol NaCl}$$

We need to convert 100.0 g of the NaCl solution to the mass of water. Since the mass of the solution is the mass of solute plus the mass of water, we write

$$100.0\ \text{g NaCl solution} = 10.0\ \text{g NaCl} + 90.0\ \text{g H}_2\text{O}$$

From this we can write the equivalence

$$100.0\ \text{g NaCl solution} \Leftrightarrow 90.0\ \text{g H}_2\text{O}$$

Then we will use the SI prefixes for the conversion of grams to kilograms.

Solution: First, we write the question as an equation,

$$\frac{10.0\ \text{g NaCl}}{100.0\ \text{g NaCl soln}} = \frac{?\ \text{mol NaCl}}{1\ \text{kg water}}$$

We can see that the logical first step will be to convert the mass of NaCl to moles. Then in two conversions we convert the mass of solution to kg of water

$$\frac{10.0\ \cancel{\text{g NaCl}}}{100.0\ \cancel{\text{g NaCl soln}}} \times \frac{1\ \text{mol NaCl}}{58.44\ \cancel{\text{g NaCl}}} \times \frac{100.0\ \cancel{\text{g NaCl soln}}}{90.0\ \cancel{\text{g water}}} \times \frac{1000\ \cancel{\text{g water}}}{1\ \text{kg water}} = 1.90\ m\ \text{NaCl}$$

We conclude that 10.0% NaCl solution would also be 1.90 molal and the supplier's product is acceptable.

Is the Answer Reasonable? A convenient rounding of the numbers in our calculation to one significant figure might be

$$\frac{10\text{ g }\cancel{\text{NaCl}}}{100\text{ g }\cancel{\text{NaCl soln}}} \times \frac{1\text{ mol NaCl}}{50\text{ g }\cancel{\text{NaCl}}} \times \frac{100\text{ g }\cancel{\text{NaCl soln}}}{100\text{ }\cancel{\text{g water}}} \times \frac{1000\text{ }\cancel{\text{g water}}}{1\text{ kg water}} = 2\ m\text{ NaCl}$$

This is close to our calculated value, and we conclude we were correct. Notice that rounding the 58.6 down to 50 compensates for rounding 90 up to 100, so our estimate is closer to the correct number. We do not need a calculator for this estimate. First, cancel five zeros from the numerator numbers and five zeros from the denominator numbers. This leaves you with 10/5 = 2.

Practice Exercises

13.9 | A bottle on the stockroom shelf reads 52% sodium hydroxide solution. What is the molality of this solution? (*Hint:* Recall that the % means (w/w) percentage.)

13.10 | A certain sample of concentrated hydrochloric acid is 37.0% HCl. Calculate the molality of this solution.

13.6 | Temperature-Dependent Concentration Units

In Chapter 5 we were introduced to molarity as a concentration unit and to its usefulness as a conversion factor.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{13.10}$$

The molarity is also temperature dependent because the denominator will change with changes in temperature. Another temperature-dependent concentration unit is the mass–volume percentage, defined as

$$\%(\text{w/v}) = \frac{\text{grams solute}}{\text{mL solution}} \times 100\% \tag{13.11}$$

Volume/volume percentages (%v/v) are also sometimes used for liquid solutions. This is the number of mL of solute in 100 mL of solution.

Conversions between the two temperature-dependent units are done in two steps: first, the numerators can be converted between moles and mass, and second, the denominators are then a simple conversion between mL and L units.

When we want to convert between a temperature-dependent concentration unit such as molarity and a temperature-independent unit such as molality, we need to know the density of the solution. Example 13.5 illustrates this method.

Example 13.5
Finding Molarity from Mass Percent

A certain supply of concentrated hydrochloric acid has a concentration of 36.0% HCl. The density of the solution is 1.19 g mL^{-1}. Calculate the molar concentration of HCl.

Analysis: Recall the definitions of percentage by mass and molarity. We must perform the following conversion:

$$\frac{36.0\text{ g HCl}}{100\text{ g HCl soln}} \quad \text{to} \quad \frac{?\text{ mol HCl}}{1\text{ L HCl soln}}$$

We have two conversions to perform. In the numerator we need to convert the mass of HCl to moles HCl, and in the denominator we convert the mass of solution to liters of solution.

Assembling the Tools: We need the mass-to-moles equality for HCl. The molar mass of HCl is 36.46, and we write the equality as

$$1.000 \text{ mol HCl} = 36.46 \text{ g HCl}$$

We use the density to write the equality

$$1.19 \text{ g solution} = 1.00 \text{ mL solution}$$

Finally, we use the SI prefixes to obtain the correct volume units.

Solution: We first write the question in equation form,

$$\frac{36.0 \text{ g HCl}}{100 \text{ g HCl soln}} = ? \frac{\text{mol HCl}}{1 \text{ L HCl soln}}$$

We can do the conversions in either order. Here, we'll convert the numerator first:

$$\frac{36.0 \text{ g } \cancel{\text{HCl}}}{100 \text{ g } \cancel{\text{HCl soln}}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g } \cancel{\text{HCl}}} \times \frac{1.19 \text{ g } \cancel{\text{HCl soln}}}{1.00 \text{ } \cancel{\text{mL HCl soln}}} \times \frac{1000 \text{ } \cancel{\text{mL HCl soln}}}{1 \text{ L HCl soln}} = 11.8 \text{ } M \text{ HCl}$$

So 36.0% HCl is also 11.8 *M* HCl.

Is the Answer Reasonable? We can estimate the answer in our head. First, cancel the 36 g HCl in the numerator and the 36.46 g HCl in the denominator to give ~1.0 (shown in red below). Now we divide 1000 in the numerator by 100 in the denominator to get 10 (shown in blue). All that is left is 1.19 × 10 = 11.9 *M* as shown below.

$$\frac{36.0}{100} \times \frac{1 \text{ mol HCl}}{36.46} \times \frac{1.19}{1.00} \times \frac{1000}{1 \text{ L HCl soln}} = 11.9 \text{ } M \text{ HCl}$$

This is very close to our calculated answer and we can be confident in our result.

Practice Exercises

13.11 | Hydrobromic acid can be purchased as 40.0% solution. The density of this solution is 1.38 g mL^{-1}. What is the molar concentration of hydrobromic acid in this solution?

13.12 | One gram of aluminum nitrate is dissolved in 1.00 liter of water at 20.0 °C. The density of water at this temperature is 0.9982 g cm^{-3} and the density of the resulting solution is 0.9989 g cm^{-3}. Calculate the molarity and molality of this solution.

Practice Exercise 13.12 illustrates that when the concentration of an aqueous solution is very low—one gram per liter, for example—the molality and the molarity are very close to the same numerical value. As a result, we can conveniently interchange molality and molarity when aqueous solutions are very dilute.

13.7 | Colligative Properties

The physical properties of solutions to be studied in this and succeeding sections are called **colligative properties**, because they depend mostly on the concentrations of particles in mixtures, not on their chemical identities. We start with an examination of the effects of solutes on the vapor pressures of solvents in liquid solutions.

■ After the Greek *kolligativ*, depending on number and not on nature.

Raoult's Law

■ Francois Marie Raoult (1830–1901) was a French scientist.

All liquid solutions of *nonvolatile* solutes (solutes that have no tendency to evaporate) have lower vapor pressures than their pure solvents. The vapor pressure of such a solution is proportional to how much of the solution actually consists of the solvent. This proportionality is given by **Raoult's law**, which says that the vapor pressure of the solution, P_{solution}, equals the mole fraction of the solvent, X_{solvent}, multiplied by its vapor pressure when pure, $P°_{\text{solvent}}$. In equation form, Raoult's law is expressed as follows.

TOOLS

Raoult's law

Raoult's Law equation

$$P_{\text{solution}} = X_{\text{solvent}}\, P°_{\text{solvent}} \tag{13.12}$$

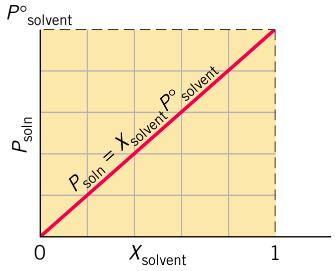


Figure 13.13 | **A Raoult's law plot.**

Because of the form of this equation, a plot of P_{solution} versus X_{solvent} should be *linear* at all concentrations when the system obeys Raoult's law (see Figure 13.13).

Notice that the mole fraction in Raoult's law refers to the solvent, not the solute. Usually we're more interested in the effect of the *solute's* mole fraction concentration, X_{solute}, on the vapor pressure. We can show that the change in vapor pressure, ΔP, is directly proportional to the mole fraction of solute, X_{solute}, as follows.[6]

$$\Delta P = X_{\text{solute}}\, P°_{\text{solvent}} \tag{13.13}$$

The change in vapor pressure equals the mole fraction of the solute times the solvent's vapor pressure when pure.

Example 13.6
Determining Vapor Pressures with Raoult's Law

Carbon tetrachloride has a vapor pressure of 155 torr at 20 °C. This solvent can dissolve candle wax, which is essentially nonvolatile. Although candle wax is a mixture, we can take its molecular formula to be $C_{22}H_{46}$ (molar mass = 311 g mol^{-1}). Without any change in temperature, by how much will the vapor pressure of CCl_4 be lowered when a solution is prepared by dissolving 10.0 g of wax in 40.0 g of CCl_4 (molar mass = 154 g mol^{-1})? What is the final vapor pressure of this solution?

■ **Analysis:** This question uses Raoult's law, which, in turn, uses mole fractions that are determined using our previously learned mole conversions. We have to work backward through this sequence to determine the change in vapor pressure of the solution. We then use that change to determine the actual vapor pressure.

---

[6] To derive Equation 13.13, note that the value of ΔP is simply the following difference.

$$\Delta P = (P°_{\text{solvent}} - P_{\text{solution}})$$

The mole fractions for our two-component system, X_{solvent} and X_{solute}, must add up to 1; it's the nature of mole fractions.

$$X_{\text{solvent}} = 1 - X_{\text{solute}}$$

We now insert this expression for X_{solvent} into the Raoult's law equation.

$$\begin{aligned} P_{\text{solution}} &= X_{\text{solvent}} P°_{\text{solvent}} \\ P_{\text{solution}} &= (1 - X_{\text{solute}}) P°_{\text{solvent}} = P°_{\text{solvent}} - X_{\text{solute}} P°_{\text{solvent}} \end{aligned}$$

So, by rearranging terms,

$$X_{\text{solute}} P°_{\text{solvent}} = P°_{\text{solvent}} - P_{\text{solution}} = \Delta P$$

This result gives us Equation 13.13.

Assembling the Tools: We will use the version of Raoult's law as given in Equation 13.13. Since we know the vapor pressure of the pure solvent, we will have to use Equation 13.8 to determine the mole fraction of the solute to determine the change in vapor pressure.

$$X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solvent}} + n_{\text{solute}}}$$

We are given the masses of the solvent and solute and can calculate the moles of each in order to use this equation. We use our mass-to-moles equalities to determine the moles of CCl_4 and $C_{22}H_{46}$.

$$1 \text{ mol } CCl_4 = 154 \text{ g } CCl_4 \qquad \text{and} \qquad 1 \text{ mol } C_{22}H_{46} = 311 \text{ g } C_{22}H_{46}$$

For the second part of the problem, we can use Raoult's law, Equation 13.12, or simply subtract the decrease in vapor pressure from the vapor pressure of pure carbon tetrachloride. The subtraction seems simpler, so we will use it.

Solution: Working backward in our analysis, we first have to determine the moles of each substance in the mixture. Our calculations are

$$\text{For } CCl_4 \qquad 40.0 \ \cancel{\text{g } CCl_4} \times \frac{1 \text{ mol } CCl_4}{154 \ \cancel{\text{g } CCl_4}} = 0.260 \text{ mol } CCl_4$$

$$\text{For } C_{22}H_{46} \qquad 10.0 \ \cancel{\text{g } C_{22}H_{46}} \times \frac{1 \text{ mol } C_{22}H_{46}}{311 \ \cancel{\text{g } C_{22}H_{46}}} = 0.0322 \text{ mol } C_{22}H_{46}$$

The total number of moles is 0.292 mol. Now we can calculate the mole fraction of the solute, $C_{22}H_{46}$,

$$X_{C_{22}H_{46}} = \frac{0.0322 \ \cancel{\text{mol}}}{0.292 \ \cancel{\text{mol}}} = 0.110$$

The amount that the vapor pressure is lowered, ΔP, will be this particular mole fraction, 0.110, times the vapor pressure of pure CCl_4 (155 torr at 20 °C), calculated by Equation 13.13.

$$\Delta P = 0.110 \times 155 \text{ torr} = 17.0 \text{ torr}$$

The presence of the wax in the CCl_4 lowers the vapor pressure of the CCl_4 by 17.0 torr. The actual vapor pressure will be 155 torr − 17 torr = 138 torr.

Is the Answer Reasonable? Our quickest check is that the vapor pressure is lowered and the amount it is lowered is approximately 10% of the original vapor pressure. Ten percent of 155 is close to our answer, 17.0 torr, and we are satisfied that it is reasonable. The last step to get the total vapor pressure is an easy subtraction.

Practice Exercises

13.13 | Dibutyl phthalate, $C_{16}H_{22}O_4$ (molar mass 278 g mol^{-1}), is an oil sometimes used to soften plastic articles. Its vapor pressure is negligible around room temperature. What is the vapor pressure, at 20.0 °C, of a solution of 20.0 g of dibutyl phthalate in 50.0 g of pentane, C_5H_{12} (molar mass 72.2 g mol^{-1})? The vapor pressure of pure pentane at 20.0 °C is 541 torr. (*Hint:* Calculate mole fractions first.)

13.14 | Acetone (molar mass = 58.0 g mol^{-1}) has a vapor pressure at a given temperature of 162 torr. At the same temperature, how many grams of nonvolatile stearic acid (molar mass = 284.5 g mol^{-1}) must be added to 156 g of acetone to decrease its vapor pressure to 155 torr?

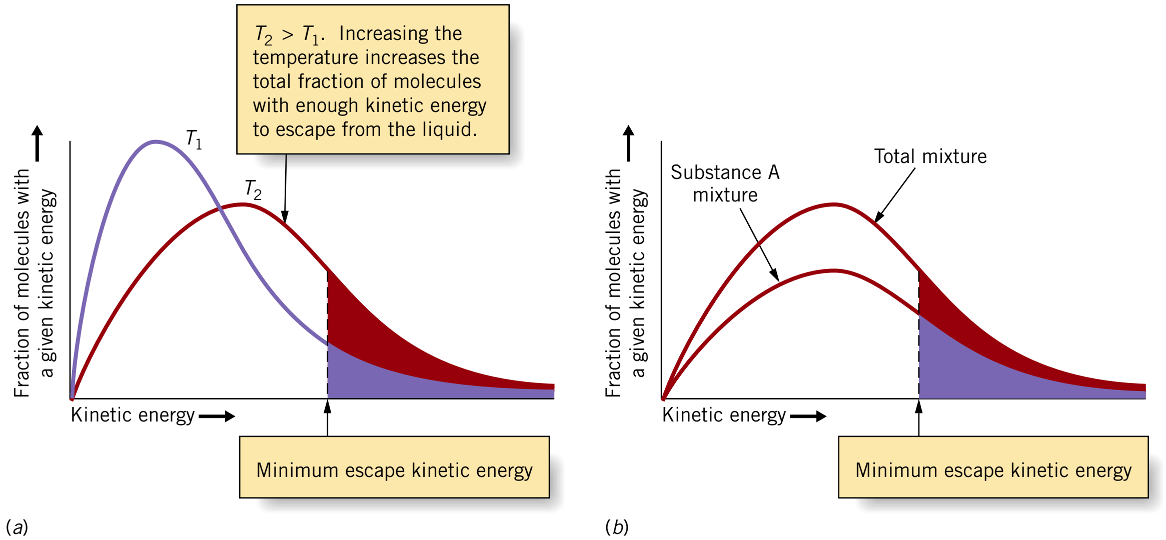


Figure 13.14 | **Kinetic energy distributions explain decreases in vapor pressure.** (*a*) Two KE distribution curves, one at a high temperature T_{high} and one at a low temperature T_{low}. The purple-shaded portion for the low temperature shows a decrease in the fraction of molecules able to escape the liquid phase compared to the purple and red areas combined for the high temperature curve. (*b*) A KE distribution curve for a mixture with a 0.333 mole fraction of nonvolatile solute mixed with the same volatile solvent as in (*a*). The purple-shaded area represents the fraction of volatile molecules able to leave the liquid phase. The purple and red areas combined represent the fraction of all molecules with that energy, but the molecules represented by the red area cannot vaporize until they achieve a much higher KE.

Raoult's Law and a Nonvolatile Solute

In Chapter 12 we saw that the vapor pressure of a volatile liquid changes with temperature. In particular, if we lower the temperature, the vapor pressure decreases. Figure 13.14*a* illustrates that the lowered vapor pressure was due to a smaller fraction of all molecules having enough energy to leave the liquid state. Figure 13.14*b* shows how a similar decrease in the fraction of energetic molecules results from the presence of a nonvolatile solute.

In Figure 13.14*b* the lower curve represents the KE distribution for the volatile part of the mixture, substance *A*, and the KE distribution for the nonvolatile substance, *B*, is added to it to obtain the upper curve that represents the KE distribution for the entire solution. We can see that the height of the lower curve is consistently 2/3 that of the upper curve. This is because we assumed a mole fraction of 0.667 for *A*. Also, the fraction of *all* molecules that exceed the kinetic energy needed by *A* to escape the solution has not changed. What has changed is that only 2/3 of those molecules are *A*—the rest are *B* and they can't escape the solution. The molecular view of this effect is shown in Figure 13.15.

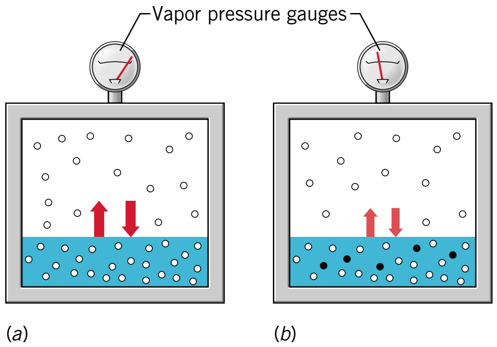


Figure 13.15 | **Molecular view of a nonvolatile solute reducing the vapor pressure of a solvent.** (*a*) Equilibrium between a pure solvent and its vapor. With a high number of solvent molecules in the liquid phase, the rate of evaporation and condensation is relatively high. (*b*) In the solution, some of the solvent molecules have been replaced with solute molecules. There are fewer solvent molecules available to evaporate from solution. The evaporation rate is lower. When equilibrium is established, there are fewer molecules in the vapor. The vapor pressure of the solution is less than that of the pure solvent.

Raoult's Law and Two Volatile Solutes

When two (or more) components of a liquid solution can evaporate, the vapor contains molecules of each. Each volatile substance contributes its own partial pressure to the total pressure. By Raoult's law, the partial pressure of a particular component is directly proportional to the component's mole fraction in the solution. By Dalton's law of partial pressures, the total vapor pressure will be the sum of all the partial pressures. To calculate these partial pressures, we use the Raoult's law equation for each component.

When component A is present in a mole fraction of X_A, its partial pressure (P_A) is this fraction of its vapor pressure when pure—namely, P_A°.

$$P_A = X_A P_A^\circ$$

By the same argument, the partial pressure of component B, is

$$P_B = X_B P_B^\circ$$

■ Remember, P_A and P_B here are the *partial* pressures as calculated by Raoult's law.

The total pressure of the solution of liquids A and B is then, by Dalton's law of partial pressures, the sum of P_A and P_B.

$$P_{\text{solution}} = X_A P_A^\circ + X_B P_B^\circ \qquad \textbf{(13.14)}$$

Raoult's law for two volatile solvents

Notice that Equation 13.14 contains the Raoult's law equation as a special case. If one component—say, component B—is nonvolatile, it has no vapor pressure (P_B° is zero) so the $X_B P_B^\circ$ term drops out, leaving the Raoult's law equation, 13.13.

Example 13.7

Calculating the Vapor Pressure of a Solution of Two Volatile Liquids

Acetone is a solvent for both water and molecular liquids that do not dissolve in water, like benzene. At 22 °C, acetone has a vapor pressure of 164 torr. The vapor pressure of water at 22 °C is 18.5 torr. Assuming that the mixture obeys Raoult's law, what would be the vapor pressure of a solution of acetone and water with 50.0 mol% of each?

■ **Analysis and Tools:** To find P_{total} we need to calculate the individual partial pressures and then add them together. Our tool is Equation 13.14.

■ **Solution:** A concentration of 50.0 mol% corresponds to a mole fraction of 0.500, so

$$\begin{aligned} P_{\text{acetone}} &= 0.500 \times 164 \text{ torr} = 82.0 \text{ torr} \\ P_{\text{water}} &= 0.500 \times 18.5 \text{ torr} = \underline{9.25 \text{ torr}} \\ P_{\text{total}} &= 91.2 \text{ torr} \end{aligned}$$

■ **Is the Answer Reasonable?** The vapor pressure of the solution (91.2 torr) has to be much higher than that of pure water (18.5 torr) because of the volatile acetone, but much less than that of pure acetone (164 torr) because of the high mole fraction of water. The answer seems reasonable.

Practice Exercises

13.15 | At 20.0 °C, the vapor pressure of cyclohexane, a nonpolar hydrocarbon, is 66.9 torr and that of toluene, a hydrocarbon related to benzene, is 21.1 torr. What is the vapor pressure of a solution of the two at 20.0 °C when toluene is present at a mole fraction of 0.250? (*Hint:* Recall that all mole fractions of the components of a mixture must add up to 1.00.)

13.16 | Using the information from Practice Exercise 13.15, calculate the expected vapor pressure of a mixture of cyclohexane and toluene that consists of 122 grams of each liquid.

Only ideal solutions obey Raoult's law exactly. The vapor pressures of real solutions are sometimes higher or sometimes lower than Raoult's law would predict. These differences between ideal and real solution behavior are quite useful. They can tell us whether the attractive forces in the pure solvents, before mixing, are stronger or weaker than the attractive forces in the mixture. Comparing experimental vapor pressures with the predictions of Raoult's law provide a simple way to compare the relative strengths of attractions between molecules in solution. When the attractions between unlike molecules in the

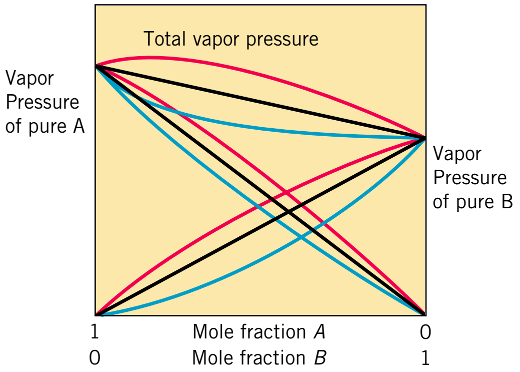


Figure 13.16 | **Vapor pressure vesus mole fraction of ideal and nonideal solutions.** Solutions are made with two volatile solvents. (*a*) The black lines represent an ideal solution, where the attractive forces in the mixture and pure liquids are the same and $\Delta H_{\text{soln}} = 0$. (*b*) Blue lines represent solutions that have an exothermic ΔH_{soln} and have stronger attractions in the mixture. (*c*) Red lines represent solutions that have an endothermic ΔH_{soln} and have weaker attractions in the mixture.

mixture are stronger than those in the pure solvents, the experimental vapor pressure will be lower than calculated with Raoult's law. Conversely, when the attractions between unlike molecules in the mixture are weaker than those in the pure solvents, the experimental vapor pressure will be larger than Raoult's law predicts.

Referring back to Figure 13.7, we can see that when attractions between the unlike molecules in the mixture are stronger than those in the pure solvents, we should expect Step 3, the mixing process, to be more exothermic than Steps 1 and 2 combined. Therefore, a lower vapor pressure than expected indicates an exothermic heat of mixing that should be easily observed as a warming of the mixture. Similarly, if the vapor pressure of the mixture is greater than expected by Raoult's law, the heat of mixing will be endothermic. Figure 13.16 illustrates the shapes of the vapor pressure versus mole fraction curves for ideal solutions and two types of nonideal solutions.

Freezing Point Depression and Boiling Point Elevation

The lowering of the vapor pressure produced by the presence of a nonvolatile solute affects both the boiling and freezing points of a solution. This is illustrated for water in Figure 13.17. In this phase diagram, the solid blue lines correspond to the three equilibrium lines in the phase diagram for pure water, which we discussed in Section 12.10. Adding a nonvolatile solute lowers the vapor pressure of the solution, giving a new liquid–vapor equilibrium line for the solution, which is shown as the red line connecting points *A* and *B*.

When the solution freezes, the solid that forms is pure ice; there is no solute within the ice crystals. This is because the highly ordered structure of the solid doesn't allow solute molecules to take the place of water molecules. As a result, both pure water and the solution have the same solid–vapor equilibrium line on the phase diagram. Point *A* on the diagram is at the intersection of the liquid–vapor and solid–vapor equilibrium lines for the

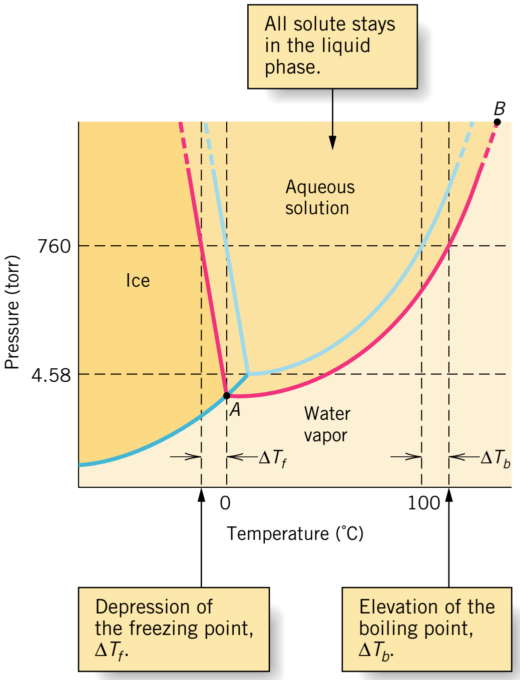


Figure 13.17 | **Phase diagrams for water and an aqueous solution.** Phase diagram for pure water (blue lines) and an aqueous solution of a nonvolatile solute (red lines).

solution and represents the new triple point for the solution. Rising from this triple point is the solid–liquid equilibrium line for the solution, shown in red.

If we look at where the solid–liquid and liquid–vapor lines cross the 1 atm (760 torr) pressure line, we can find the normal freezing and boiling points. For water (the blue lines), the freezing point is 0 °C and the boiling point is 100 °C. Notice that the solid–liquid line for the solution meets the 760 torr line at temperatures *below* 0 °C. In other words, the freezing point of the solution is below that of pure water. The amount by which the freezing point is lowered is called the **freezing point depression** and is given the symbol ΔT_f. Similarly, we can see that the liquid–vapor line for the solution crosses the 760 torr line at a temperature *above* 100 °C, so the solution boils at a higher temperature than pure water. The amount by which the boiling point is raised is called the **boiling point elevation**. It is given the symbol ΔT_b.

■ Recall that the definition of the normal boiling and freezing points specifies that the pressure is 1 atm.

Freezing point depression and boiling point elevation are both colligative properties. The magnitudes of ΔT_f and ΔT_b are proportional to the concentration of solute and solvent molecules. Molality (m) is the preferred concentration expression (rather than mole fraction or percent by mass) because of the resulting simplicity of the equations relating ΔT to concentration. The following equations work reasonably well only for dilute solutions, however.

$$\Delta T_f = K_f m \tag{13.15}$$

$$\Delta T_b = K_b m \tag{13.16}$$

TOOLS

Freezing point depression; boiling point elevation

K_f and K_b are proportionality constants and are called, respectively, the **molal freezing point depression constant** and the **molal boiling point elevation constant**. The values of both K_f and K_b are characteristic of each solvent (see Table 13.3). The units of each constant are °C m^{-1}. Thus, the value of K_f for a given solvent corresponds to the number of degrees of freezing point lowering for each molal unit of concentration. The K_f for water is 1.86 °C m^{-1}. A 1.00 m solution in water freezes at 1.86 °C *below* the normal freezing point of 0.00 °C, or at −1.86 °C. A 2.00 m solution should freeze at −3.72 °C. (We say "should" because systems are seldom this ideal.) Similarly, because K_b for water is 0.51 °C m^{-1}, a 1.00 m aqueous solution at 1 atm pressure boils at (100.00 + 0.51) °C or 100.51 °C, and a 2.00 m solution should boil at 101.02 °C.

Table 13.3 Molal Boiling Point Elevation and Freezing Point Depression Constants

Solvent	BP (°C)	K_b (°C m^{-1})	MP (°C)	K_f (°C m^{-1})
Water	100	0.51	0	1.86
Acetic acid	118.3	3.07	16.6	3.90
Benzene	80.2	2.53	5.45	5.07
Chloroform	61.2	3.63	−63.5	4.68
Camphor	—	—	178.4	39.7
Cyclohexane	80.7	2.69	6.5	20.2

Example 13.8
Estimating a Freezing Point Using a Colligative Property

Estimate the freezing point, at 1.0 atm, of a solution made from 10.0 g of urea, $CO(NH_2)_2$ (molar mass 60.06 g mol^{-1}), and 125 g of water.

■ **Analysis:** We need to use the appropriate equation for the freezing point depression. To use that equation we need to use the appropriate calculations to determine the molality of the solution.

Assembling the Tools: The main tool we need is expressed in Equation 13.15, the freezing point depression. We can look up the value for K_f and write the expression as

$$\Delta T_f = (1.86\ ^\circ\text{C}\ m^{-1})\ m$$

The equation for molality is

$$m = \frac{\text{mol urea}}{\text{kg water}}$$

and we use the molar mass of urea to convert the mass to the moles we need.

Solution: We write the equation that needs to be solved.

$$\Delta T_f = (1.86\ ^\circ\text{C molal}^{-1})\ m$$

Now to start the process for determining the molality, we'll convert grams of urea to moles.

$$10.0\ \cancel{\text{g CO(NH}_2)_2} \times \frac{1 \text{ mol CO(NH}_2)_2}{60.06\ \cancel{\text{g CO(NH}_2)_2}} = 0.166 \text{ mol CO(NH}_2)_2$$

and the 125 g to 0.125 kg of water. The molality is calculated as

$$\text{molality} = \frac{0.166 \text{ mol}}{0.125 \text{ kg}} = 1.33\ m$$

Now we solve the freezing point depression problem using the molality we just determined.

$$\begin{aligned}\Delta T_f &= (1.86\ ^\circ\text{C}\ \cancel{m^{-1}})(1.33\ \cancel{m}) \\ &= 2.47\ ^\circ\text{C}\end{aligned}$$

The solution should freeze at 2.47 °C below 0 °C, or at −2.47 °C.

Is the Answer Reasonable? For every unit of molality, the freezing point must be depressed by about 2 °C. The molality of this solution is between 1 m and 2 m, so we expect the freezing point depression to be between about 2 °C and 4 °C.

Practice Exercises

13.17 | In making candy, a certain recipe calls for heating an aqueous sucrose solution to the "soft-ball" stage, which has a boiling point of 235–240 °F. What is the range of mass percentages of the solutions of sugar ($C_{12}H_{22}O_{11}$) that boil at those two temperatures? (*Hint:* Remember that temperature changes are in °C.)

13.18 | How many grams of glucose (molar mass = 180.9 g mol^{-1}) must be dissolved in 255 g of water to raise the boiling point to 102.36 °C?

Determining Molar Masses

We have described freezing point depression and boiling point elevation as *colligative* properties; they depend on the relative *numbers* of particles, not on their kinds. Because the effects are proportional to molal concentrations, experimentally measured values of ΔT_f or ΔT_b can be useful for calculating the molar masses of unknown solutes. To do this, let's examine the molality part of the temperature change in Equations 13.15 and 13.16 more closely. If we expand the molality equation we get

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{\left(\dfrac{\text{g solute}}{\text{molar mass solute}}\right)}{\text{kg solvent}}$$

This indicates that if we measure ΔT_f or ΔT_b and know the mass of solute in each kg of solvent, we can estimate the last remaining unknown, the molar mass. Example 13.9 shows how to estimate molar mass.

Example 13.9

Calculating a Molar Mass from Freezing Point Depression Data

A solution made by dissolving 5.65 g of an unknown molecular compound in 110.0 g of benzene froze at 4.39 °C. What is the molar mass of the solute?

- **Analysis:** To calculate the molar mass (i.e., g mol^{-1}), we need to know two things about the same sample: the number of moles and the number of grams. In this example, we've been given the number of grams, and we have to use the remaining data to calculate the number of moles. We will need to expand the molarity part of the freezing point depression equation to do this, as suggested previously.

- **Assembling the Tools:** Our basic tool is the freezing point depression equation 13.15.

$$\Delta T_f = K_f m$$

We will also use the definition of molality

$$m = \frac{\text{mol solute}}{\text{kg solvent}} \quad \text{and} \quad \text{mol solute} = \frac{\text{g solute}}{\text{molar mass solute}}$$

along with the expanded form for ΔT_f,

$$\Delta T_f = T_{f\text{ pure}} - T_{f\text{ observed}}$$

- **Solution:** Table 13.3 tells us that the melting point of pure benzene is 5.45 °C and that the value of K_f for benzene is 5.07 °C m^{-1}. The amount of freezing point depression is

$$\Delta T_f = 5.45\ ^\circ\text{C} - 4.39\ ^\circ\text{C} = 1.06\ ^\circ\text{C}$$

We now use Equation 13.15 to find the molality of the solution,

$$\Delta T_f = K_f m$$

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.06\ ^\circ\text{C}}{5.07\ ^\circ\text{C}\ m^{-1}} = 0.209\ m$$

This means that for every kilogram of benzene in the solution, there are 0.209 mol of solute. However, we have only 110.0 g or 0.1100 kg of benzene, so the actual number of moles of solute in the given solution is

$$0.1100\ \text{kg benzene} \times \frac{0.209\ \text{mol solute}}{1\ \text{kg benzene}} = 0.0230\ \text{mol solute}$$

We can now obtain the molar mass. There are 5.65 g of solute and 0.0230 mol of solute. Using the expression for calculating moles of solute we can write

$$0.0230\ \text{mol solute} = \frac{5.65\ \text{g solute}}{\text{molar mass solute}}$$

With a simple rearrangement,

$$\text{molar mass solute} = \frac{5.65\ \text{g solute}}{0.0230\ \text{mol solute}} = 246\ \text{g mol}^{-1}$$

The mass of one mole of the solute is 246 g.

Is the Answer Reasonable? A common mistake to avoid is using the given value of the freezing point, 4.39 °C, in Equation 13.15, instead of calculating ΔT_f. A check shows that we *have* calculated ΔT_f correctly. The ratio of ΔT_f to K_f is about 1/5, or 0.2 *m*, which corresponds to a ratio of 0.2 mol solute per 1 kg of benzene. The solution prepared has only 0.1 kg of solvent, so to have the same ratio, the amount of solute must be about 0.02 mol (2×10^{-2} mol). The sample weighs about 5 g, and dividing 5 g by 2×10^{-2} mol gives 2.5×10^{2} g/mol, or 250 g/mol. This is very close to the answer we obtained, so we can feel confident it's correct.

Practice Exercises

13.19 | A solution made by dissolving 3.46 g of an unknown compound in 85.0 g of benzene froze at 4.13 °C. What is the molar mass of the compound? (*Hint:* Recall the equation for calculating moles of a substance to find the key relationship.)

13.20 | A mixture is prepared that is 5.0 %(w/w) of an unknown substance mixed with naphthalene (molar mass = 128.2 g mol^{-1}). The freezing point of this mixture is found to be 77.3 °C. What is the molar mass of the unknown substance? (The melting point of naphthalene is 80.2 °C and $K_f = 6.9$ °C m^{-1}.)

Osmosis

In living things, membranes of various kinds keep mixtures and solutions organized and separated. Yet some substances have to be able to pass through membranes so that nutrients and products of chemical work can be distributed correctly. These membranes, in other words, must have a selective *permeability*. They must keep some substances from going through while letting others pass. Such membranes are said to be *semipermeable.*

The degree of permeability varies with the kind of membrane. Cellophane, for example, is permeable to water and small solute particles—ions or molecules—but impermeable to very large molecules, like those of starch or proteins. Special membranes can even be prepared that are permeable only to water, not to any solutes.

Depending on the kind of membrane separating solutions of different concentrations, two similar phenomena, *dialysis* and *osmosis*, can be observed. Both are functions of the relative concentrations of the particles of the dissolved materials on each side of the membrane. Therefore, physical properties of these systems are also classified as colligative properties.

When a membrane is able to let both water and *small* solute particles through, such as the membranes in living systems, the process is called **dialysis**, and the membrane is called a **dialyzing membrane**. It does not permit huge molecules through, like those of proteins and starch. Artificial kidney machines use dialyzing membranes to help remove the smaller molecules of wastes from the blood while letting the blood retain its large protein molecules.

When a semipermeable membrane will let only solvent molecules get through, this movement is called *osmosis*, and the special membrane needed to observe it is called an **osmotic membrane**.

When **osmosis** occurs, there's a net shift of solvent across the membrane from the more dilute solution (or pure solvent) into the more concentrated solution. This happens because there is a tendency toward the equalization of concentrations between the two solutions in contact with one another across the membrane. The rate of passage of solvent molecules through the membrane into the more concentrated solution is greater than their rate of passage in the opposite direction, presumably because at the surface of the membrane the solvent concentration is greater in the more dilute solution (Figure 13.18*a*). This leads to a gradual net flow of water through the membrane into the more concentrated solution.

We observe an effect similar to osmosis if two solutions with unequal concentrations of a nonvolatile solute are placed in a sealed container (Figure 13.18*b*). The rate of evaporation

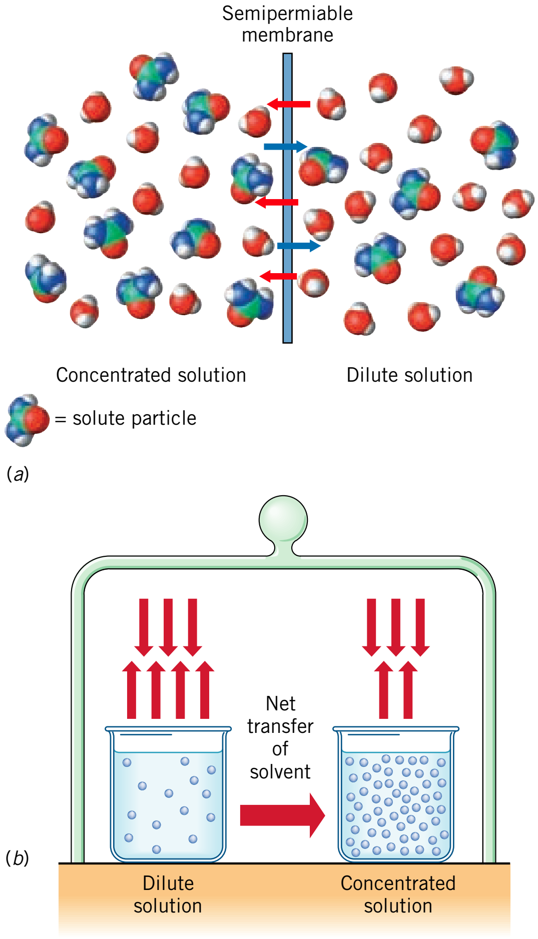


Figure 13.18 | **Principles at work in osmosis.** (*a*) Osmosis. Solvent molecules pass more frequently from the more dilute solution into the more concentrated one, as indicated by the arrows. This leads to a gradual transfer of solvent from the less concentrated solution into the more concentrated one. (*b*) Because the two solutions have unequal rates of evaporation, but the same rate of condensation, there is a gradual net transfer of solvent from the more dilute solution into the more concentrated one.

from the more dilute solution is greater than that of the more concentrated solution, but the rate of return to each is the same because both solutions are in contact with the same gas phase. As a result, neither solution is in equilibrium with the vapor. In the dilute solution, molecules of solvent are evaporating faster than they're condensing. In the concentrated solution, however, just the opposite occurs; more water molecules return to the solution than leave it. Therefore, over time there is a gradual net transfer of solvent from the dilute solution into the more concentrated one until they both achieve the same concentration and vapor pressure.

Osmotic Pressure

An osmosis experiment is illustrated in Figure 13.19. Initially, we have a solution (*B*) in a tube fitted with an osmotic membrane that dips into a container of pure water (*A*). As time passes, the volume of liquid in the tube increases as solvent molecules transfer into the solution. In Figure 13.19*b*, the net transport of water into the solution has visibly increased the volume.

The weight of the rising fluid column in Figure 13.19*b* provides a push or opposing pressure that makes it increasingly more difficult for molecules of water to enter the solution inside the tube. Eventually, this pressure becomes sufficient to stop the osmosis. The exact opposing pressure needed to prevent any osmotic flow *when one of the liquids is pure solvent* is called the **osmotic pressure** of the solution. If we apply further pressure, as illustrated in Figure 13.19*c*, we can force enough water back through the membrane to restore the system to its original condition.

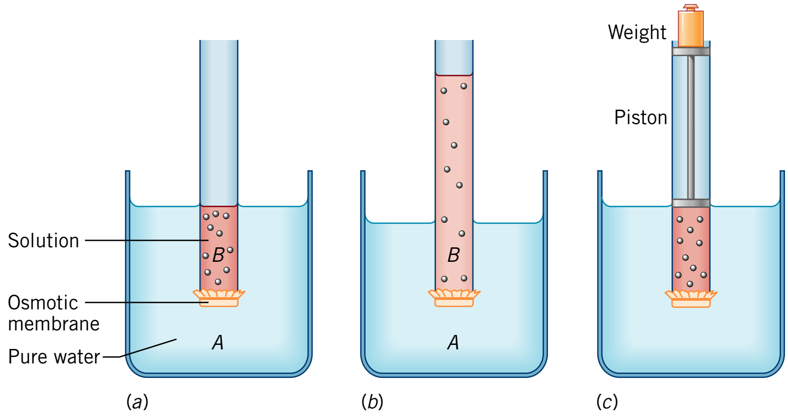


Figure 13.19 | **Osmosis and osmotic pressure.** (*a*) Initial conditions. A solution, *B*, is separated from pure water, *A*, by an osmotic membrane; no osmosis has yet occurred. (*b*) After a while, the volume of fluid in the tube has increased visibly. Osmosis has taken place. (*c*) A back pressure is needed to prevent osmosis. The amount of back pressure is called the osmotic pressure of the solution.

■ Reverse osmosis systems are available for home use at hardware stores. They can be installed to remove impurities and foul tastes from drinking water. Some bottled water available on supermarket shelves contains water that's been purified by reverse osmosis.

Notice that the term "osmotic pressure" uses the word *pressure* in a novel way. Apart from osmosis, a solution does not "have" a special pressure called osmotic pressure. What the solution has is a *concentration* that can generate the occurrence of osmosis and the associated osmotic pressure under the right circumstances. Then, in proportion to the solution's concentration, a specific back pressure is required to prevent osmosis. By *exceeding* this back pressure, osmosis can be reversed. **Reverse osmosis** is widely used to purify seawater, both on ocean-going ships and in arid locations where fresh water is scarce, polluted, or unavailable. (See more details in Chemistry and Current Affairs.)

The symbol for osmotic pressure is the Greek capital pi, Π. In a dilute aqueous solution, Π is proportional both to temperature, T, and molar concentration of the solute in the solution, M:

$$\Pi \propto MT$$

The proportionality constant turns out to be the gas constant, R, so for a *dilute* aqueous solution we can write

$$\Pi = MRT \tag{13.17}$$

TOOLS

Osmotic pressure

Of course, M is the ratio mol/L, which we can write as n/V, where n is the number of moles and V is the volume in liters. If we replace M with n/V in Equation 13.17 and rearrange terms, we have an equation for osmotic pressure identical in form to the ideal gas law.

$$\Pi V = nRT \tag{13.18}$$

Equation 13.18 is the *van't Hoff equation for osmotic pressure*.

Osmotic pressure is of tremendous importance in biology and medicine. Cells are surrounded with membranes that restrict the flow of salts but allow water to pass through freely. To maintain a constant amount of water, the osmotic pressure of solutions on either side of the cell membrane must be identical. For an example, a solution that is 0.85% NaCl by mass has the same osmotic pressure as the contents of red blood cells, and red blood cells bathed in this solution can maintain their normal water content. The solution is said to be *isotonic* with red blood cells. Blood plasma is an isotonic solution.

If the cell is placed in a solution with a salt concentration higher than the concentration within the cell, osmosis causes water to flow out of the cell. Such a solution is said to be *hypertonic*. The cell shrinks and dehydrates, and eventually dies. This process kills freshwater fish and plants that are washed out to sea.

CHEMISTRY AND CURRENT AFFAIRS 13.1

Pure Water by Reverse Osmosis

Many important issues face the world today, but none is more important than the availability of potable (pure and drinkable) water. As Table 1 shows, almost 97% of all water is saltwater found in the oceans and seas. Most of the freshwater is tied up in polar and glacier ice.

Table 1 Water Resources

Water Source	Amount in the World	Amount per Person
All water	1.4×10^9 km^3	0.2 km^3
Freshwater total	3.9×10^7 km^3	5.6×10^6 m^3
Freshwater, icebound	3.3×10^7 km^3	4.8×10^6 m^3
Freshwater, liquid	6.0×10^6 km^3	8.6×10^5 m^3

The average person in a developed country uses approximately 54 m^3 of water per year. While it seems that there may be plenty of water—the problem is availability. Temperate climates get plenty of rain and usually have adequate water in lakes, streams, and aquifers. However, temperate climates often have high population densities, resulting in high water usage along with a greater possibility of water pollution. In arid regions, water is scarce even though the populations may be small. In all cases, natural water is a valuable resource that may have to be augmented using available technology.

There are many technologies that can be used to obtain freshwater. Boiling and condensing water uses too much energy to be practical. However, very large scale, multi-stage vacuum distillation produces about 85% of the desalinized water in the world but requires significant energy input. Reverse osmosis uses less energy and can be designed for smaller applications. Other methods such as ion-exchange, electrodialysis, freezing, and solar dehumidification are also used.

Osmosis, as described in this chapter, involves spontaneous movement of pure solvent (usually water) through a membrane into a solution containing a solute. The tendency of the solvent to move through the membrane is measured as the osmotic pressure. To reverse the flow of water through an osmotic membrane, a pressure that exceeds the osmotic pressure needs to be applied to the solution side of the membrane. The result will be pure water extracted from a solution such as seawater. Figure 1 shows a schematic diagram of a reverse osmosis process. Figure 2 is a photo of a bank of reverse osmosis separation tubes in operation.

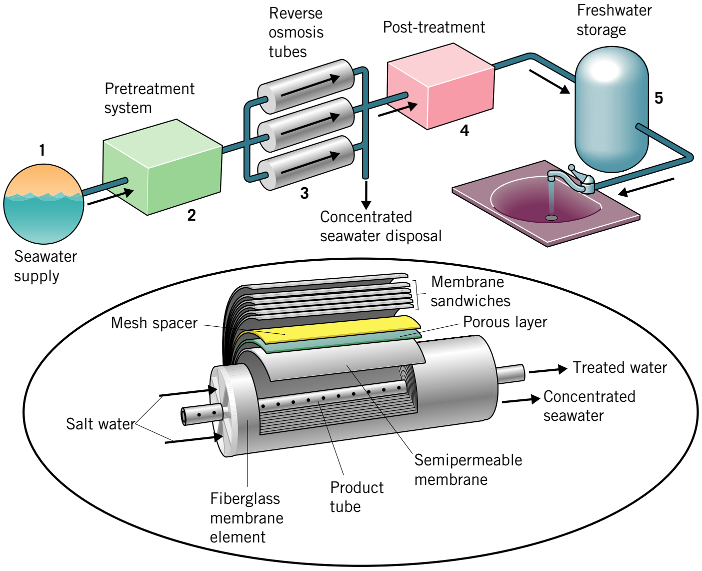

Reverse osmosis tubes
Post-treatment
Freshwater storage
Pretreatment system
1
2
3
4
5
Seawater supply
Concentrated seawater disposal
Membrane sandwiches
Mesh spacer
Porous layer
Treated water
Concentrated seawater
Salt water
Semipermeable membrane
Product tube
Fiberglass membrane element

Figure 1 A schematic diagram of a reverse osmosis process. (1) The seawater is filtered (2) to remove virtually all particulate matter. (3) Pressure is applied to perform the separation. (4) Purified water is treated to adjust the acidity and add anti-bacterial agents before (5) storage. *Inset:* A diagram of the construction of the reverse osmosis tube.

Figure 2 A commercial reverse osmosis unit. *(iStockphoto)*

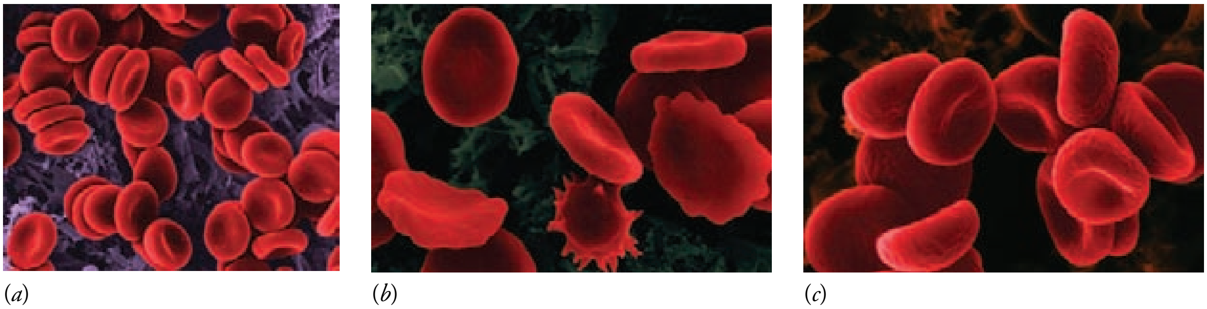


Figure 13.20 | **Effects of isotonic, hypertonic, and hypotonic solutions on red blood cells.** (*a*) In an isotonic solution (0.85% NaCl by mass), solutions on either side of the membrane have the same osmotic pressure, and there is no flow of water across the cell membrane. (*b*) In this hypertonic solution (5.0% NaCl by mass), water flows from areas of lower salt concentration (inside the cell) to areas of higher concentration (the hypertonic solution), causing the cell to dehydrate. (*c*) In this hypotonic solution (0.1% NaCl by mass), water flows from areas of lower salt concentration (the hypotonic solution) to areas of higher concentration (inside the cell). The cell swells and bursts. *(a: Dennis KunkelMicroscopy, Inc./VisualsUnlimited; b, c: Dr. Dennis Kunkel /VisualsUnlimited)*

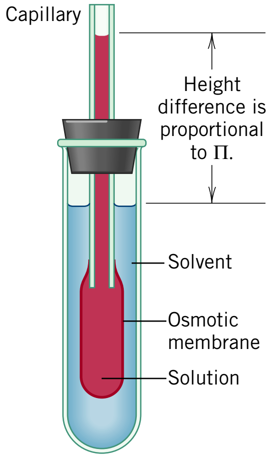


Figure 13.21 | **Simple osmometer.** When solvent moves into the solution by osmosis, the level of the solution in the capillary rises. The height reached can be related to the osmotic pressure of the solution.

On the other hand, water will flow into the cell if it is placed into a solution with an osmotic pressure that is much lower than the osmotic pressure of the cell's contents. Such a solution is called a *hypotonic* solution. A cell placed in distilled water, for example, will swell and burst. If you've ever tried to put in a pair of contact lenses with tap water instead of an isotonic saline solution, you've experienced cell damage from a hypotonic solution. The effects of isotonic, hypotonic, and hypertonic solutions on cells are shown in Figure 13.20.

Obviously, the measurement of osmotic pressure can be very important in preparing solutions that will be used to culture tissues or to administer medicines intravenously. Osmotic pressures can be measured by an instrument called an *osmometer*, illustrated and explained in Figure 13.21. Osmotic pressures can be very high, even in dilute solutions, as Example 13.10 shows.

Example 13.10
Calculating Osmotic Pressure

A very dilute solution, 0.00100 *M* sucrose in water, is separated from pure water by an osmotic membrane. What osmotic pressure in torr develops at 25 °C or 298 K?

■ **Analysis:** This question involves the application of the appropriate form of the osmotic pressure equation. Of course, we must be sure to use the correct value of *R*, so that the units work out correctly.

■ **Assembling the Tools:** We need to use Equation 13.17,

$$\Pi = MRT$$

Since we are given the temperature in kelvins and molarity has units of moles and liters, it is appropriate to choose $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$.

■ **Solution:** Substituting into Equation 13.17, being sure to use the temperature in kelvins so the units cancel correctly,

$$\begin{aligned}\Pi &= (0.00100 \cancel{\text{mol}}\ \cancel{\text{L}^{-1}})(0.0821 \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(298 \cancel{\text{K}}) \\ &= 0.0245 \text{ atm}\end{aligned}$$

In torr we have

$$\Pi = 0.0245\ \cancel{\text{atm}} \times \frac{760\ \text{torr}}{1\ \cancel{\text{atm}}} = 18.6\ \text{torr}$$

The osmotic pressure of 0.00100 M sugar in water is 18.6 torr.

■ **Is the Answer Reasonable?** A 1 M solution should have an osmotic pressure of RT. Rounding the gas law constant to 0.08 and the temperature to 300, the osmotic pressure of a 1 M solution should be about 24 atm. The osmotic pressure of an 0.001 M solution should be 1/1000 of this, or about 0.024 atm, which is very close to what we got before we converted to torr.

Practice Exercises

13.21 | What is the osmotic pressure, in mm Hg and mm H_2O, of a protein solution when 5.00 g of the protein (molar mass = 235,000 g mol^{-1}) is used to prepare 100.0 mL of an aqueous solution at 4 °C? (*Hint:* The units needed for this calculation are specified by the value of R that is used.)

13.22 | What is the osmotic pressure in torr of a 0.0115 M glucose solution at body temperature (37 °C)? What are the boiling and freezing points for the same solution?

In the preceding example, you saw that a 0.0010 M solution of sugar has an osmotic pressure of 18.6 torr, which is equivalent to 18.6 mm Hg. This pressure is sufficient to support a column of the solution (which is mostly water) roughly 25 cm or 10 in high. If the solution had been 100 times as concentrated, 0.100 M sugar—(about the same as 1/4 of a teaspoon of sugar in your tea)—the height of the column supported would be roughly 25 m or over 80 ft! Osmotic pressure is one of several mechanisms by which water can reach the top of very tall trees.

Determining Molar Mass

An osmotic pressure measurement taken of a dilute solution can be used to determine the molar concentration of the solute, regardless of its chemical composition. Knowledge of the molarity, along with the mass of the solute in the solution, permits us to calculate the molar mass.

Determination of molar mass by osmotic pressure is much more sensitive than determination by the freezing point depression or boiling point elevation methods. The following example illustrates how osmotic pressure experiments can be used to determine molar mass.

Example 13.11

Determining Molar Mass from Osmotic Pressure

An aqueous solution with a volume of 100.0 mL and containing 0.122 g of an unknown molecular compound has an osmotic pressure of 16.0 torr at 20.0 °C. What is the molar mass of the solute?

■ **Analysis:** As we noted in Example 13.9, to determine a molar mass we need to measure two quantities for the same sample: its mass and the number of moles. Then, the molar mass is the ratio of grams to moles. We're given the number of *grams* of the solute, so we need to find the number of *moles* equivalent to this mass in order to compute the ratio.

■ **Assembling the Tools:** We can use the osmotic pressure Equation 13.18,

$$\Pi V = nRT$$

to calculate the number of moles, n. We need to convert the given pressure to 0.0211 atm. The temperature, 20.0 °C, corresponds to 293 K (273 + 20.0) and the volume of 100.0 mL corresponds to 0.1000 L. Since we are given the mass, we just need the definition of molar mass as the tool to complete the calculation.

■ $16.0\ \text{torr} \times \dfrac{1\ \text{atm}}{760\ \text{torr}} = 0.0211\ \text{atm}$

Solution: First, the number of moles, n, is calculated using the Equation 13.18 (with the data we just converted to the correct units),

$$(0.0211\ \cancel{\text{atm}})(0.1000\ \cancel{\text{L}}) = (n)(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(293\ \cancel{\text{K}})$$

$$n = 8.77 \times 10^{-5}\text{mol}$$

The molar mass of the solute is the number of grams of solute per mole of solute:

$$\text{Molar mass} = \frac{0.122\ \text{g}}{8.77 \times 10^{-5}\ \text{mol}} = 1.39 \times 10^{3}\ \text{g mol}^{-1}$$

Is the Answer Reasonable? In using Equation 13.18, it is essential that the pressure be in atmospheres when using $R = 0.0821$ L atm mol^{-1} K^{-1}. If all the units cancel correctly (and they do), we've computed the number of moles correctly. The moles of solute is approximately 10×10^{-5}, or 1×10^{-4}. Dividing the mass, roughly 0.12 g, by 1×10^{-4} mol gives 0.12×10^{4} g per mol or 1.2×10^{3} g per mol, which is close to the value we found.

Practice Exercises

13.23 | Estimate the molecular mass of a protein when 137.2 mg of the protein, dissolved in 100.0 mL of water at 4 °C, supports a column of water that is 6.45 cm high. (*Hint:* The answer should be very large. Don't forget to convert cm of water to atmospheres of pressure.)

13.24 | A solution of a carbohydrate prepared by dissolving 72.4 mg in 100 mL of solution has an osmotic pressure of 25.0 torr at 25.0 °C. What is the molecular mass of the compound?

Colligative Properties of Ionic Solutes

The molal freezing point depression constant for water is 1.86 °C m^{-1}. So you might think that a 1.00 m solution of NaCl would freeze at −1.86 °C. Instead, it freezes at −3.37 °C. This greater depression of the freezing point by the salt, which is almost twice 1.86 °C, is not hard to understand if we remember that colligative properties depend on the concentrations of *particles*. We know that NaCl(*s*) dissociates into ions in water.

$$\text{NaCl}(s) \longrightarrow \text{Na}^{+}(aq) + \text{Cl}^{-}(aq)$$

If the ions are truly separated, 1.00 m NaCl actually has a concentration of dissolved solute particles that is 2.00 m, twice the given molal concentration. Theoretically, 1.00 m NaCl should freeze at $2 \times 1.00\ m \times (-1.86\ °\text{C}\ m^{-1})$ or −3.72 °C. (Why it actually freezes a little higher than this, at −3.37 °C, will be discussed shortly.)

If we made up a solution of 1.00 m $(\text{NH}_4)_2\text{SO}_4$, we would have to consider the following dissociation.

$$(\text{NH}_4)_2\text{SO}_4(s) \longrightarrow 2\text{NH}_4{}^{+}(aq) + \text{SO}_4{}^{2-}(aq)$$

One mole of $(\text{NH}_4)_2\text{SO}_4$ can give a total of 3 mol of ions (2 mol of $\text{NH}_4{}^{+}$ and 1 mol of $\text{SO}_4{}^{2-}$). We would expect the freezing point of a 1.00 m solution of $(\text{NH}_4)_2\text{SO}_4$ to be $3 \times 1.00\ m \times (-1.86\ °\text{C}\ m^{-1}) = -5.58\ °\text{C}$.

When we want to roughly *estimate* a colligative property of a solution of an electrolyte, we recalculate the solution's molality using an assumption about the way the solute dissociates or ionizes. For example, with ionic substances we may assume 100% dissociation, although we will see shortly that this assumption is only true for very dilute solutions.

Example 13.12

Estimating the Freezing Point of a Salt Solution

Estimate the freezing point of aqueous 0.106 m MgCl_2, assuming that it dissociates completely.

Analysis: Equation 13.15 relates a change in freezing temperature to molality, but we now have to include the fact that our solute dissociates into three particles, one Mg^{2+} and two Cl^- ions. Including this additional information allows us to make a better estimate of the freezing point.

Assembling the Tools: We will use the basic freezing point equation, with the K_f for water from Table 13.3.

$$\Delta T_f = (1.86\ ^\circ\text{C}\ m^{-1})\ m$$

However, our molality must be the molality of all ions, not the molality of the salt.

$$\text{MgCl}_2(s) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{Cl}^-(aq)$$

Solution: Because 1 mol of $MgCl_2$ gives 3 mol of ions, the effective (assumed) molality of ions in the solution is three times the molality of the salt, 0.106 *m*.

$$\text{Effective molality} = (3)(0.106\ m) = 0.318\ m$$

The effective molarity is often called the osmolarity in the biological sciences.

Now we can use Equation 13.15.

$$\begin{aligned}\Delta T_f &= (1.86\ ^\circ\text{C}\ m^{-1})(0.318\ m)\\ &= 0.591\ ^\circ\text{C}\end{aligned}$$

The freezing point is depressed below 0.000 °C by 0.591 °C, so we calculate that this solution freezes at −0.591 °C.

Is the Answer Reasonable? The molality of particles, as recalculated, is roughly 0.3, so 3/10th of 1.86 (call it 2) is about 0.6, which, after we add the unit, °C, and subtract from 0 °C gives −0.6 °C, which is close to the answer.

Practice Exercises

13.25 | Calculate the freezing point of aqueous 0.237 *m* LiCl on the assumption that it is 100% dissociated. Calculate the freezing point if the percent dissociation is 0%. (*Hint:* Recall the relationships developed in Section 13.7.)

13.26 | Determine the freezing point of aqueous solutions of $MgSO_4$ that are (a) 0.100 *m*, (b) 0.0100 *m*, and (c) 0.00100 *m*. Which of these could be measured with your laboratory thermometer that is graduated in one °C intervals?

Analyzing and Solving Multi-Concept Problems

A sample of a recently synthesized compound was analyzed by a technician but the analysis of the data is left to you. The technician took 15.00 mL of the substance, which has a density of 1.106 g/mL, and burned it in an excess of oxygen. The carbon dioxide collected weighed 28.63 grams and the water collected weighed 11.71 grams. In another experiment, 1.395 g of the compound was decomposed by heating strongly in the presence of metallic sodium to destroy the organic material and release any chlorine as chloride ions. Those chloride ions are precipitated with silver nitrate and the result is 2.541 g of AgCl. Finally, 5.41 g of this compound were mixed with 85.0 g of benzene and the freezing point was found to be 3.33 °C. What is the formula for the compound?

Analysis We need to determine the empirical formula for the compound and then the molecular formula. Since several methods were used for the analysis, we should calculate the percent composition of the compound, then the empirical formula, and finally the molecular formula. To summarize, for the first part we will use the analytical data to compute the percentage of each element in the compound. In the second part we determine the empirical formula. In the third part we find the molar mass from the freezing point depression. The fourth part will be the determination of the actual formula.

PART 1

Assembling the Tools We need to use the available data to determine the percentage of carbon, hydrogen, and chlorine in the compound. The percentages are calculated as follows:

$$\%\ \text{composition} = \frac{\text{mass of element}}{\text{mass of sample}} \times 100\%$$

We determine the mass of sample from the volume by using the density as a conversion factor as described in Chapter 2. Then we can use the stoichiometric conversions in Chapter 4.

Solution Our first step is to convert the volume of our sample to the mass, using the density,

$$15.00\ \cancel{\text{mL}} \times \frac{1.106\ \text{g}}{1\ \cancel{\text{mL}}} = 16.59\ \text{g sample}$$

Next we can convert the mass of CO_2 to the mass of carbon,

$$28.63\ \cancel{\text{g CO}_2} \times \frac{12.011\ \text{g C}}{44.01\ \cancel{\text{g CO}_2}} = 7.807\ \text{g C}$$

and convert the mass of H_2O to the mass of H,

$$11.71\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.015\ \cancel{\text{g H}_2\text{O}}} \times \frac{2\ \cancel{\text{mol H}}}{1\ \cancel{\text{mol H}_2\text{O}}} \times \frac{1.008\ \text{g H}}{1\ \cancel{\text{mol H}}} = 1.310\ \text{g H}$$

We then calculate the percentage of C and H

$$\%\ \text{C} = \frac{7.807\ \text{g C}}{16.59\ \text{g sample}} \times 100\% = 47.06\%\ \text{C}$$

$$\%\ \text{H} = \frac{1.310\ \text{g H}}{16.59\ \text{g sample}} \times 100\% = 7.900\%\ \text{H}$$

The mass of chlorine is calculated as

$$2.541\ \cancel{\text{g AgCl}} \times \frac{1\ \cancel{\text{mol AgCl}}}{143.32\ \cancel{\text{g AgCl}}} \times \frac{1\ \cancel{\text{mol Cl}}}{1\ \cancel{\text{mol AgCl}}} \times \frac{35.45\ \text{g Cl}}{1\ \cancel{\text{mol Cl}}} = 0.6285\ \text{g Cl}$$

The percentage of chloride in the sample is

$$\%\text{Cl} = \frac{0.6285\ \text{g Cl}}{1.395\ \text{g sample}} \times 100\% = 45.04\%\ \text{Cl}$$

The percentages add up to almost 100%, and we can conclude that there are no other elements in the compound except C, H, and Cl.

PART 2

Assembling the Tools We convert the percentages to mass units, assuming a 100 g sample. Next, we use the stoichiometric conversions from mass to moles for the elements in the compound. Last, we use the procedures in Section 4.3 to determine the empirical formula.

Solution We will convert the percentages to mass and then to moles for the three elements,

$$47.06\ \cancel{\text{g C}} \times \frac{1\ \text{mol C}}{12.011\ \cancel{\text{g C}}} = 3.918\ \text{mol C}$$

$$7.900\ \cancel{\text{g H}} \times \frac{1\ \text{mol H}}{1.008\ \cancel{\text{g H}}} = 7.837\ \text{mol H}$$

$$45.04\ \cancel{\text{g Cl}} \times \frac{1\ \text{mol Cl}}{35.45\ \cancel{\text{g Cl}}} = 1.271\ \text{mol Cl}$$

We divide each of the quantities above by the smallest value, 1.271, to get

$$3.04\ \text{mol C},\quad 6.17\ \text{mol H},\quad \text{and}\quad 1.00\ \text{mol Cl}$$

These numbers are close enough to integers to write

$$3 \text{ mol C}, \quad 6 \text{ mol H}, \quad \text{and} \quad 1 \text{ mol Cl}$$

The empirical formula is C_3H_6Cl.

PART 3

Assembling the Tools We need to determine the molar mass from the freezing point depression, Equation 13.15. The freezing point of pure benzene from Table 13.3 is 5.45 °C and the freezing point depression constant is 5.07 °C m^{-1}. We can calculate the molality, then the molar mass.

Solution The measured freezing point is 3.33 °C and ΔT_f is 2.12 °C. Using Equation 13.15 we write

$$\Delta T_f = 2.12\ °\text{C} = (5.07\ °\text{C}\ m^{-1})\ m$$

The molality is 0.418.

We can expand the definition of molality as

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg solvent}} = \frac{\text{g solute/molar mass solute}}{\text{kg solvent}}$$

Entering the known data we get

$$0.418\ m = \frac{5.41 \text{ g solute/molar mass of solute}}{0.085 \text{ kg solvent}}$$

and the molar mass of the solute is

$$\text{molar mass of solute} = \frac{5.41 \text{ g solute}}{0.085 \text{ kg solvent} \times 0.418\ m} = 152.2 \text{ g mol}^{-1}$$

PART 4

Assembling the Tools Now we need to determine the molecular formula using the method described in Section 4.3. We need to take the molar mass of the molecular formula and divide it by the molar mass of the empirical formula to determine how many empirical formula units are in the complete molecular formula.

Solution We divide the molar mass by the empirical formula mass, and the result should be a small whole number that is the multiplication factor for the formula's subscripts,

$$\frac{152.2}{77.5} = 1.96 = 2$$

Therefore, we multiply all of the subscripts in the empirical formula by 2 and get the formula $C_6H_{12}Cl_2$.

Are the Answers Reasonable? In a four-part problem, if we end up with a simple, whole-number ratio after many calculations, it gives us confidence that the preceding parts were correct. Looking more closely at the first part, the percentage of hydrogen is the smallest, as we expect for the lightest element. In Part 2 we get numbers that are very close to whole-number ratios for the formula. In Part 3 we find a molar mass that is neither extremely small or large, as expected for a freezing point depression experiment. Each part seems to have reasonable results, and we are confident that the final result is correct.

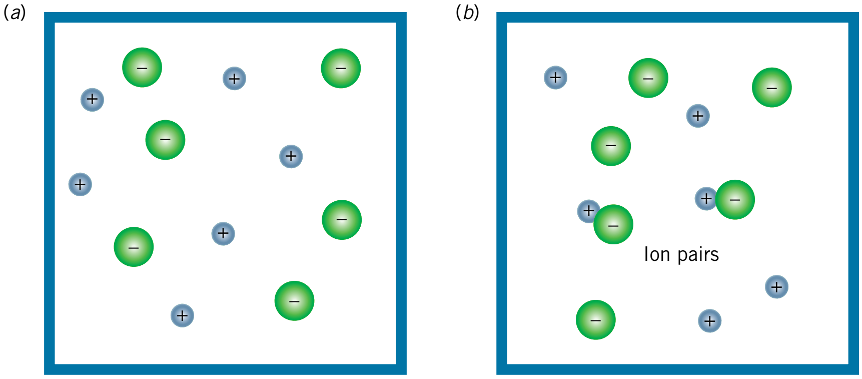


Figure 13.22 | **Ion pairs in a solution of NaCl.** (*a*) If NaCl were completely dissociated in water, the Na^+ and Cl^- ions would be totally independent. (*b*) Interionic attractions cause some ions to group together as ion pairs, which reduces the total number of independent particles in the solution. In this diagram, two ion pairs are shown. (Water molecules are not shown for clarity.)

Ion Pairing

Experiments show that neither the 1.00 *m* NaCl nor the 1.00 *m* $(NH_4)_2SO_4$ solution described earlier in this section freezes quite as low as calculated. Our assumption that an electrolyte separates *completely* into its ions is incorrect. Some oppositely charged ions exist as very closely associated pairs, called **ion pairs**, which behave as single "molecules" (Figure 13.22). Clusters larger than two ions probably also exist. The formation of ion pairs and clusters makes the actual *particle* concentration in a 1.00 *m* NaCl solution somewhat less than 2.00 *m*. As a result, the freezing point depression of 1.00 *m* NaCl is not quite as large as calculated on the basis of 100% dissociation.

■ "Association" is the opposite of dissociation. It is the coming together of particles to form larger particles.

As solutions of electrolytes are made more and more *dilute*, the observed and calculated freezing points come closer and closer together. At greater dilutions, the **association** (coming together) of ions is less and less a complication because the ions collide less frequently, resulting in relatively fewer ion pairs. Generally, solutes behave more and more as if they were 100% separated into their ions in ever more dilute solutions.

Chemists compare the degrees of dissociation of electrolytes at different dilutions by a quantity called the **van't Hoff factor, *i*.** It is the ratio of the observed freezing point depression to the value calculated on the assumption that the solute dissolves as a nonelectrolyte.

$$i = \frac{(\Delta T_f)_{\text{measured}}}{(\Delta T_f)_{\text{calculated as a nonelectrolyte}}}$$

The predicted van't Hoff factor, *i*, is 2 for NaCl, KCl, and $MgSO_4$, which break up into two ions on 100% dissociation. For K_2SO_4, the theoretical value of *i* is 3 because one K_2SO_4 unit gives 3 ions. The actual van't Hoff factors for several electrolytes at different dilutions are given in Table 13.4. Notice that with decreasing concentration (that is, at higher dilutions) the experimental van't Hoff factors agree better with their corresponding hypothetical van't Hoff factors.

The increase in the percentage dissociation that comes with greater dilution is not the same for all salts. In going from concentrations of 0.1 to 0.001 *m*, the increase in percentage dissociation of KCl, as measured by the change in *i*, is only about 7%. However, for K_2SO_4 the increase for the same dilution is about 22%, a difference caused by the anion, SO_4^{2-}. It has twice the charge as the anion in KCl, and so the SO_4^{2-} ion attracts K^+ more strongly than can Cl^-. Hence, letting an ion of 2− charge and an ion of 1+ charge get farther apart by dilution has a greater effect on their acting independently than giving ions of 1− and 1+ charge more room. When *both* cation and anion are doubly charged, the improvement in percent dissociation with dilution is even greater. We can see from Table 13.4 that there is an almost 50% increase in the value of *i* for $MgSO_4$ as we go from a 0.1 to a 0.001 *m* solution.

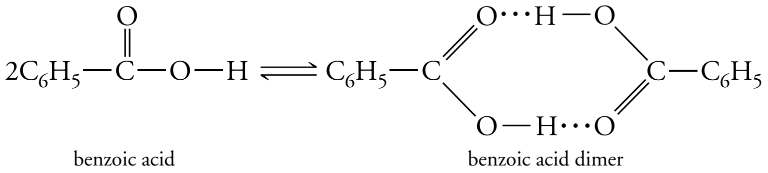
Table 13.4 Van't Hoff Factors versus Concentration

	Van't Hoff Factor, *i*			
	Molal Concentration (mol salt/kg water)			
Salt	0.1	0.01	0.001	Value of *i* if 100% Dissociation Occurred
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

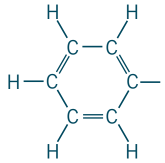
Molecular Association

Some molecular solutes produce *weaker* colligative effects than their molal concentrations would lead us to predict. These unexpectedly weak colligative properties are often evidence that solute molecules are clustering or associating in solution. For example, when dissolved in benzene, benzoic acid molecules associate as **dimers**. They are held together by hydrogen bonds, indicated by the dotted lines in the following equation.

■ *Di-* signifies two, so a dimer is the result of the combination of two single molecules.



■ C_6H_5–, called the phenyl group in organic chemistry, has the structure



Because of association, the depression of the freezing point of a 1.00 *m* solution of benzoic acid in benzene is only about one-half the calculated value. By forming a dimer, benzoic acid has an effective molecular mass that is twice as much as normally calculated. The larger effective molecular mass reduces the molal concentration of particles by half, and the effect on the freezing point depression is reduced by one-half.

13.8 | Heterogeneous Mixtures

Up to now we have discussed true solutions, mixtures that have a single phase and are uniform throughout. Heterogeneous mixtures, often called **dispersions**, have two or more phases or are not homogeneous. These are very important chemically since many industrial reactions can be described as heterogeneous and because many consumer products are dispersions of various types. We will consider two types of these dispersions, **suspensions** and **colloids**.

Suspensions

A suspension is characterized by the presence of relatively large particles mixed in a solvent. To prepare such a suspension, a substance can be mixed uniformly in a solvent, or dispersing medium, by mechanical means such as mixing or shaking. However, once the mixing process is stopped, the particles in a suspension will start to coalesce, due to attractive forces, into large particles that will separate into two phases. In other suspensions, such as fine sand dispersed in water, the two phases separate due to gravitational forces.

You may be most familiar with suspensions as common drugs. Solid magnesium hydroxide is suspended in water in a preparation called milk of magnesia. Many antibiotics are aqueous suspensions that you must "shake well before dispensing." Some salad dressings, such as those shown in the opening photograph, fall into the same category and will separate quickly into oil and vinegar layers soon after shaking. The settling process in some suspensions can be accelerated by centrifugation where the gravitational forces are increased many-fold by the high-speed rotation of the centrifuge.

Suspensions involving the gas phase are also familiar. Soot from fires is one example.[7] The result often is a layer of black grime that covers everything outdoors. Dust, some of which is ascribed to meteorites, that settles out of the air and fine droplets of water within a fog are examples of a solid and a liquid suspended in the gas phase respectively. Air bubbles within whipped cream or whipped egg whites are examples of a suspension of a gas in a liquid that will eventually separate, if not eaten first. In whipped cream and egg whites, the suspensions are relatively long lasting; the high viscosity hinders the ability of the gas bubbles to coalesce and form separate phases.

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[7] Coal- and oil-fired power plants used to be the major sources of soot and other particulates. Modern electrostatic precipitators and scrubbers remove a large majority of these particulates.

Colloids

When the particles in a suspension are very small, Brownian motion (see Section 3.6) keeps them from settling. These mixtures that do not settle, or separate into different phases, are called colloidal dispersions. Generally a colloid particle must have at least one dimension in the range of 1 to 1000 nm. Some of the particles of water in fog and soot in smoke, mentioned previously, qualify as true colloidal substances and do not separate. A small amount of starch dissolved in water is an example of a colloid in an aqueous system, also called a sol. Table 13.5 lists examples of colloidal mixtures and classifies them based on the dispersed phase (i.e., the colloid) and the dispersing phase (the solvent). In many mixtures the sizes of colloidal particles makes them invisible to the naked eye. Although a colloidal mixture may look very much like a true solution, the colloidal particles, with dimensions similar to the wavelengths of visible light, will scatter light. This scattering is called the **Tyndall effect** and can be observed by shining a narrow beam of light through the colloidal mixture. A dramatic illustration of the Tyndall effect is shown in Figure 13.23, where red laser light shines through a series of test tubes.

■ John Tyndall, 1820–1893, a prominent physicist, succeeded Michael Faraday as the Fullerian Professor of Chemistry at the Royal Institution of Great Britain.

Figure 13.23 shows us some colloidal mixtures that look like true solutions. However, other colloidal dispersions, called **emulsions,** may look more like milk or whipped cream. In an emulsion the dispersing phase is a liquid and, often, the concentration of colloidal particles is very high. This means that colloidal particles may have a greater probability of colliding and coalescing, eventually into two phases.

Chemists have devised a variety of strategies to slow or even stop the coalescing of colloidal particles in emulsions. In recent chapters we have learned that we can reduce the frequency of collisions in the liquid phase by (a) lowering the temperature, (b) raising the viscosity, or (c) decreasing attractive forces and increasing repulsive forces. Let's look at an example of each.[8] Old-time ice cream is an emulsion of milk, eggs, cream, sugar, and flavorings. In the case of ice cream, it is kept frozen and the colloidal particles rarely collide. In the whipped cream example, the usually fluid cream has colloidal-size air bubbles incorporated into it, resulting in a very viscous product. Once again, the limited mobility of the colloidal particles keeps them from coalescing. Figure 13.24 illustrates the microscopic view of two types of emulsion: mayonnaise, a liquid–liquid emulsion, and margarine, a liquid–solid emulsion.

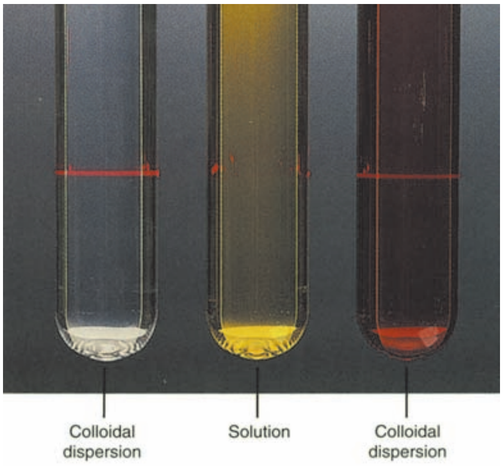

Figure 13.23 | **The Tyndall effect.** Colloidal solutions may appear as true solutions. The first tube contains a colloidal starch dispersion, the second is a true solution of Na_2CrO_4, and the third tube is a colloidal dispersion of Fe_2O_3. A red laser beam passes through all three tubes, and the colloidal dispersions scatter the red light towards the viewer while the true solution does not. *(OPC, Inc.)*

Table 13.5 Colloidal Systems

Type	Dispersed Phase[a]	Dispersing Medium	Common Examples
Foam	Gas	Liquid	Soapsuds, whipped cream
Solid foam	Gas	Solid	Pumice, marshmallow
Liquid Aerosol	Liquid	Gas	Mist, fog, clouds, air pollutants
Emulsion	Liquid	Liquid	Cream, mayonnaise, milk
Solid emulsion	Liquid	Solid	Butter, cheese
Smoke	Solid	Gas	Dust, particulates in smog, aerogels
Sol (Colloidal Dispersion)	Solid	Liquid	Starch in water, paint, jellies[b]
Solid sol	Solid	Solid	Alloys, pearls, opals

[a] Colloidal particles are in the dispersed phase.

[b] Semisolid or semirigid sols, such as gelatins and jellies, are called gels.

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[8] Each of these examples actually uses a combination of all three strategies, but we focus on the main concept for each one.

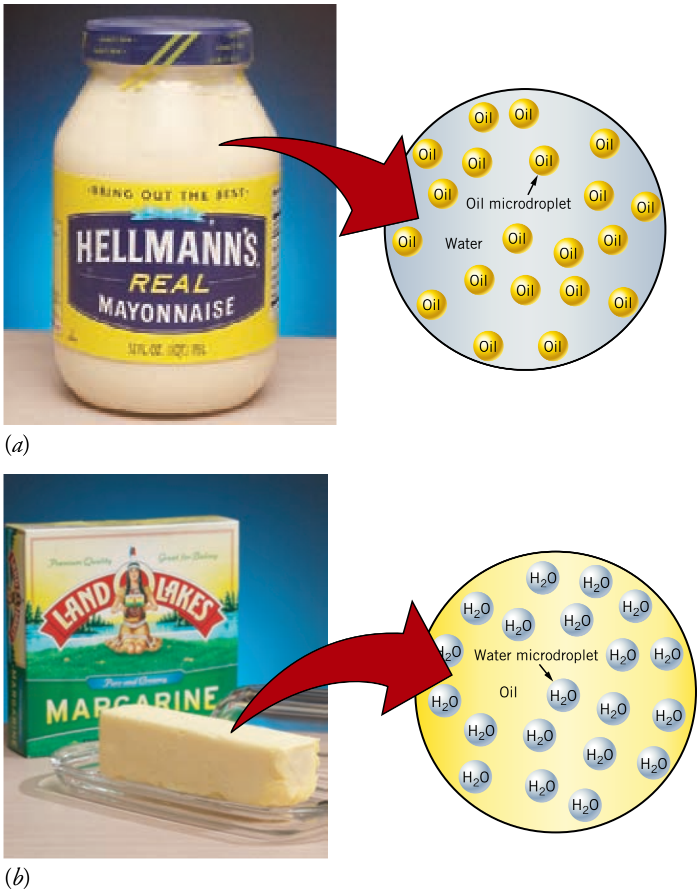


Figure 13.24 | **Two common emulsions.** (*a*) The dispersion of oil in water occurs when mayonnaise is prepared. (*b*) Low-calorie and low-fat butter is often made by dispersing water in the solid butterfat. *(Andy Washnik)*

The major method for stabilizing most commercial emulsions is to incorporate into one or both phases an electrical charge that keeps the colloidal particles apart. Surfactants such as sodium stearate are long molecules with a charged end and an uncharged hydrocarbon end. The charged end will dissolve in water and is said to be **hydrophilic**, while the hydrocarbon end dissolves more readily in oils and is called **hydrophobic.** When sodium stearate is added to an oil–water emulsion the hydrophobic end dissolves in the oil while the hydrophilic end extends into the aqueous phase. The result is often a spherical, negatively charged particle called a **micelle**. The negative charge of one micelle repels the negative charges of other micelles. The result is that micelles will not coalesce into separate oil and water phases. Proteins can also adsorb to oil particles and provide a charged surface. Figure 13.25 illustrates how adsorbed layers can produce charged colloidal particles. An emulsion stabilized in this fashion can be separated into two phases by adding an acid or base to neutralize the charged groups. This is called “breaking” an emulsion.

In crystals of small inorganic molecules a stabilizing charged layer can be established by an excess of one of the crystal’s ions. For example, if lead(II) ions are precipitated with a large excess of chloride ions, the excess chloride ions will adsorb to the surface of the lead(II) chloride crystals in what is called the primary adsorbed layer. Since the primary adsorbed layer consists of chloride ions that have a negative charge, the tiny colloidal particles will not coalesce into larger crystals that can be collected by filtration. Figure 13.25 can also be used to visualize this system. Although stabilizing an emulsion is often a desired result in commercial preparations, here we see that it may also be a problem. The effect of the adsorbed layer can be minimized by having only a small excess of chloride ions during precipitation.

Modern nanoscience is very interested in nanometer-size particles that have unusual properties. Colloidal gold is a nanoparticle that may be useful for drug delivery to tumors. Interestingly, colloidal gold was first used by medieval artists who transcribed elegantly “illuminated” bibles, where this nanoparticle exhibits many different colors. Colloidal, magnetic, iron particles have many interesting properties, as do the fullerenes, substances related to the C_{60} allotrope of carbon that we discuss in Chapter 10 on page 457.

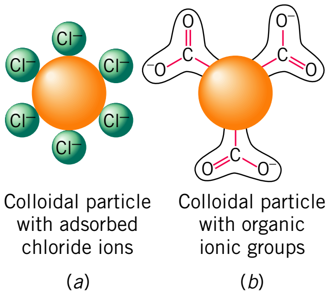

Cl^-
O
C
O^-
Colloidal particle with adsorbed chloride ions
(a)
Colloidal particle with organic ionic groups
(b)

Figure 13.25 | **Stabilizing colloidal dispersions.** Colloidal particles that may tend to coalesce can be stabilized by acquiring an electrical charge. (*a*) Inorganic precipitates can have an adsorbed layer of ions that prevents them from coalescing into particles that can be filtered. (*b*) Colloidal particles can have charged groups that give it an overall electrical charge, or charged particles can be adsorbed to the surface of a colloidal particle with the same effect.

Summary

Solutions. Polar or ionic solutes generally dissolve well in polar solvents such as water. Nonpolar, molecular solutes dissolve well in nonpolar solvents. These observations are behind the "**like dissolves like**" **rule**. Nature's driving force for establishing the more statistically probable mixed state and intermolecular attractions are the two major factors in the formation of a solution. When both solute and solvent are nonpolar, nature's tendency toward the more probable mixed state dominates because intermolecular attractive forces are weak. Ion–dipole attractions and the **solvation** or **hydration** of dissolved species are major factors in forming solutions of ionic or polar solutes in something polar, like water.

Heats of Solution. The **molar enthalpy of solution** of a solid in a liquid, also called the **heat of solution,** is calculated as the **lattice energy** subtracted from the **solvation energy** (or, when water is the solvent, the **hydration energy**). The lattice energy is the decrease in the potential energy of the system that would occur if the molecules or ions of the solute came together to form the solid solute crystals. The solvation energy corresponds to the potential energy lowering that occurs in the system from the subsequent attractions of these particles to the solvent molecules as intermingling occurs.

When liquids dissolve in liquids, an **ideal solution** forms if the potential energy increase needed to separate the molecules equals the energy lowering as the separated molecules come together. Usually, some net energy exchange occurs, however, because few solutions are ideal.

When a gas dissolves in a gas, the energy cost to separate the particles is virtually zero, because they're already separated. They remain separated in the gas mixture, so the net enthalpy of solution is very small if not zero. When a gas dissolves in an organic solvent, the solution process is often endothermic. When a gas dissolves in water, the solution process is often exothermic.

Pressure and Gas Solubility. At pressures not too much different from atmospheric pressure, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas—**Henry's law**.

Concentration Expressions. To study and use colligative properties, a solution's concentration ideally is expressed either in mole fractions or as a **molal concentration,** or **molality**. The **molality** of a solution, m, is the ratio of the number of moles of solute to the kilograms of *solvent* (not solution, but solvent). **Mass fractions** and **mass percents** are concentration expressions used often for chemicals when direct information about number of moles of solutes is not considered important. Mole fraction, molality, and mass percent are temperature-independent concentration expressions.

Colligative Properties. **Colligative properties** are those that depend on the ratio of the particles of the solute to the molecules of the solvent. These properties include the **lowering of the vapor pressure,** the **depression of a freezing point,** the **elevation of a boiling point,** and the **osmotic pressure** of a solution.

According to **Raoult's law,** the vapor pressure of a solution of a nonvolatile (molecular) solute is the vapor pressure of the pure solvent times the mole fraction of the solvent. An alternative expression of this law is that the *change* in vapor pressure caused by the solute equals the mole fraction of the solute times the pure solvent's vapor pressure. When the components of a solution are volatile liquids, then Raoult's law calculations find the *partial pressures* of the vapors of the individual liquids. The sum of the partial pressures equals the total vapor pressure of the solution.

An *ideal solution* is one that would obey Raoult's law exactly and in which all attractions between molecules are equal. An ideal solution has $\Delta H_{\text{soln}} = 0$. Heats of solution of nonideal mixtures may be exothermic or endothermic and these correspond to vapor pressures that are less or greater than expected from Raoult's law, respectively.

In proportion to its molal concentration, a solute causes a **freezing point depression** and a **boiling point elevation.** The proportionality constants are the **molal freezing point depression constant** and the **molal boiling point elevation constant,** and they differ from solvent to solvent. Freezing point and boiling point data from a solution made from known masses of both solute and solvent can be used to calculate the molecular mass of a solute.

When a solution is separated from the pure solvent (or from a less concentrated solution) by an *osmotic membrane*, **osmosis** occurs, which is the net flow of solvent into the more concentrated solution. The back pressure required to prevent osmosis is called the solution's **osmotic pressure,** which, in a dilute aqueous solution, is proportional to the product of the Kelvin temperature and the molar concentration. The proportionality constant is R, the ideal gas constant, and the equation relating these variables is $\Pi = MRT$.

When the membrane separating two different solutions is a *dialyzing membrane*, it permits **dialysis,** the passage not only of solvent molecules but also of small solute molecules or ions. Only very large molecules are denied passage.

Colligative Properties of Electrolytes. Because an electrolyte releases more ions in solution than indicated by the molal (or molar) concentration, a solution of an electrolyte has more pronounced colligative properties than a solution of a molecular compound at the same concentration. The dissociation of a strong electrolyte approaches 100% in very dilute solutions, particularly when both ions are singly charged. Weak electrolytes provide solutions more like those of nonelectrolytes.

The ratio of the value of a particular colligative property (e.g., ΔT_f) to the value expected if there were no dissociation is the **van't Hoff factor, i.** A solute whose formula unit breaks into two ions, like NaCl or $MgSO_4$, would have a van't Hoff factor of 2 if it were 100% dissociated. Observed van't Hoff factors are less than the theoretical values because of the formation of **ion pairs,** brought about by **association** of ions in solution. The van't Hoff factors approach those corresponding to 100% dissociation only as the solutions are made more and more dilute.

Heterogeneous Mixtures. **Suspensions** are mixtures where the particles are so large that they begin precipitation or coalescing as soon as the mixing process is stopped. The result is the formation of two or more phases. **Colloidal mixtures** are composed of particles with the largest dimension being 1000 nm. Colloidal mixtures do not settle and can be identified using the **Tyndall effect**. A special colloidal mixture called an **emulsion** is a mixture that can be stabilized by electrical charges or **hydrophobic** and **hydrophilic repulsions.** These factors keep the phases from coalescing. **Hydrophobic** and **hydrophilic** properties of surfactants often create **micelles** that stabilize emulsions.

TOOLS

Tools for Problem Solving

The compilation below lists the tools you have learned in this chapter that are applicable to problem solving. Review them if necessary, and refer to them when working on the Review Problems that follow.

"Like dissolves like" rule (page 587)

This rule uses the polarity and strengths of attractive forces, along with chemical composition and structure, to predict whether two substances can form a solution.

Henry's law (page 595)

The solubility of a gas at a given pressure can be approximated from its solubility at another pressure by using the Henry's law equation.

$$C_{\text{gas}} = k_{\text{H}}P_{\text{gas}}$$

Mass fraction; percentage by mass (page 597)

These concentration terms may be used as conversion factors as well as representing the concentration of a solution

$$\text{mass fraction} = \frac{\text{mass of solute}}{\text{mass of solution}}$$

$$\text{percentage by mass} = \%(\text{w/w}) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Molal concentration (page 599)

Molality is a temperature-independent concentration expression, often used in experiments where the temperature may be varied.

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Raoult's law (page 604)

Raoult's law predicts the effect of a nonvolatile solute on the vapor pressure of a solution.

$$P_{\text{solution}} = X_{\text{solvent}}P^{\circ}_{\text{solvent}}$$

A second form of Raoult's law is used when two volatile solutes, A and B, are mixed (page 607).

$$P_{\text{solution}} = X_A P^{\circ}_A + X_B P^{\circ}_B$$

Freezing point depression and boiling point elevation (page 609)

The freezing point depression and boiling point elevation equations can be used to estimate the changes in freezing and boiling points, respectively. They also provide a method for determining molar masses of non-dissociating solutes.

$$\text{Freezing point depression:} \quad \Delta T_f = K_f m$$

$$\text{Boiling point elevation:} \quad \Delta T_b = K_b m$$

Osmotic pressure (page 614)

The osmotic pressure of a solution can be used to calculate molecular masses from osmotic pressure and concentration data. Note the similarity to the ideal gas law (page 491).

$$\Pi V = nRT \quad \text{or} \quad \Pi = MRT$$

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Why Solutions Form

13.1 Why do two gases spontaneously mix when they are brought into contact?

13.2 When substances form liquid solutions, what two factors are involved in determining the solubility of the solute in the solvent?

13.3 Methanol, CH_3OH, and water are miscible in all proportions. What does this mean? Explain how the OH unit in methanol contributes to this.

13.4 Hexane (C_6H_{12}) and water are immiscible. What does this mean? Explain why they are immiscible in terms of structural features of their molecules and the forces of attraction between them.

13.5 Explain how ion–dipole forces help to bring potassium chloride into solution in water.

13.6 Explain why potassium chloride will not dissolve in carbon tetrachloride, CCl_4.

Heat of Solution

13.7 The value of ΔH_{soln} for a soluble compound is, say, $+26\ \text{kJ mol}^{-1}$, and a nearly saturated solution is prepared in an insulated container (e.g., a coffee cup calorimeter). Will the system's temperature increase or decrease as the solute dissolves?

13.8 Referring to Question 13.7, which value for this compound would be numerically larger, its lattice energy or its hydration energy?

13.9 Which would be expected to have the larger hydration energy, Al^{3+} or Li^{+}? Why? (Both ions are about the same size.)

13.10 Suggest a reason why the value of ΔH_{soln} for a gas such as CO_2, dissolving in water, is negative.

13.11 The value of ΔH_{soln} for the formation of an acetone–water solution is negative. Explain this in general terms using intermolecular forces of attraction.

13.12 The value of ΔH_{soln} for the formation of an ethanol–hexane solution is positive. Explain this in general terms that involve intermolecular forces of attraction.

13.13 When a certain solid dissolves in water, the solution becomes cool. Is ΔH_{soln} for this solute positive or negative? Explain your reasoning. Is the solubility of this substance likely to increase or decrease with increasing temperature? Explain your answer using Le Châtelier's principle.

13.14 If the value of ΔH_{soln} for the formation of a mixture of two liquids *A* and *B* is zero, what does this imply about the relative strengths of *A*–*A*, *B*–*B*, and *A*–*B* intermolecular attractions?

Temperature and Solubility

13.15 If a saturated solution of NH_4NO_3 at 75 °C is cooled to 15 °C, how many grams of solute will separate if the quantity of the solvent is 125 g? (Use the data in Figure 13.10.)

13.16 Anglers know that on hot summer days, the largest fish will be found in deep sinks in lake bottoms. Use the temperature dependence of the density of water and the temperature dependence of the oxygen solubility in water to explain why.

Pressure and Solubility

13.17 What is Henry's law?

13.18 Mountain streams often contain fewer living things than equivalent streams at sea level. Give one reason why this might be true in terms of oxygen solubilities at different pressures.

13.19 Why is ammonia so much more soluble in water than nitrogen? Would you expect hydrogen chloride gas to have a high or low solubility in water? Explain your answers to both questions.

13.20 Why does a bottled carbonated beverage fizz when you take the cap off?

Expressions of Concentration

13.21 Write the definition for each of the following concentration units: **(a)** mole fraction, **(b)** mole percent, **(c)** molality, **(d)** percent by mass. What are the maximum possible values for the units in **(a)**, **(b)**, and **(d)**?

13.22 How does the molality of a solution vary with increasing temperature? How does the molarity of a solution vary with increasing temperature?

13.23 Suppose a 1.0 *m* solution of a solute is made using a solvent with a density of 1.15 g/mL. Will the molarity of this solution be numerically larger or smaller than 1.0? Justify your conclusion mathematically.

Colligative Properties

13.24 What specific fact about a physical property of a solution must be true to call it a colligative property?

13.25 What kinds of data would have to be obtained to find out whether a solution of two miscible liquids is almost exactly an ideal solution?

13.26 When octane is mixed with methanol, the vapor pressure of the octane over the solution is higher than what we would calculate using Raoult's law. Why? Explain the discrepancy in terms of intermolecular attractions.

13.27 Explain why a nonvolatile solute dissolved in water makes the system have **(a)** a higher boiling point than water, and **(b)** a lower freezing point than water.

13.28 Why do we call dialyzing and osmotic membranes *semipermeable*? What is the opposite of *permeable*?

13.29 What is the key difference between dialyzing and osmotic membranes?

13.30 At a molecular level, explain why, in osmosis, there is a net migration of solvent from the side of the membrane less concentrated in solute to the side more concentrated in solute.

13.31 Two glucose solutions of unequal molarity are separated by an osmotic membrane. Which solution will *lose* water, the one with the higher molarity or the one with the lower molarity?

13.32 Which aqueous solution has the higher osmotic pressure, 10% glucose, $C_6H_{12}O_6$, or 10% sucrose, $C_{12}H_{22}O_{11}$? (Both are molecular compounds.)

13.33 When a solid is *associated* in a solution, what does this mean? What difference does it make to expected colligative properties?

13.34 What is the difference between a *hypertonic* solution and a *hypotonic* solution?

Colligative Properties of Electrolytes

13.35 Why are colligative properties of solutions of ionic compounds usually more pronounced than those of solutions of molecular compounds of the same molalities?

13.36 What is the van't Hoff factor? What is its expected value for all nondissociating molecular solutes? If its measured value is slightly larger than 1.0, what does this suggest about the solute? What is suggested by a van't Hoff factor of approximately 0.5?

13.37 Which aqueous solution, if either, is likely to have the higher boiling point, 0.50 *m* NaI or 0.50 *m* Na_2CO_3?

Heterogeneous Mixtures

13.38 Determine whether each of the following is likely to be a true solution, a suspension, or a colloidal mixture: **(a)** orange juice, **(b)** apple juice, **(c)** perfume, **(d)** tea, **(e)** tea with lemon juice, **(f)** canned gravy. If you have a laser pointer, how can you confirm your answers?

13.39 Can sodium stearate stabilize a water in oil emulsion? Explain your conclusion.

13.40 Addition of a neutral salt to a colloidal precipitate such as the $BaSO_4(s)$ described in the text allows the crystals to grow in size. Develop a hypothesis on why this occurs.

13.41 What is a micelle, and why does it form?

Review Problems

Heat of Solution

13.42 Consider the formation of a solution of aqueous potassium chloride. Write the thermochemical equations for **(a)** the conversion of solid KCl into its gaseous ions and **(b)** the subsequent formation of the solution by hydration of the ions. The lattice energy of KCl is -715 kJ mol^{-1}, and the hydration energy of the ions is -686 kJ mol^{-1}. Calculate the enthalpy of solution of KCl in kJ mol^{-1}.

OH **13.43** For an ionic compound dissolving in water, $\Delta H_{\text{soln}} = -56$ kJ mol^{-1} and the hydration energy is -894 kJ mol^{-1}. Estimate the lattice energy of the ionic compound.

Henry's Law

OH **13.44** The solubility of methane, the chief component of natural gas, in water at 20.0 °C and 1.0 atm pressure is 0.025 g L^{-1}. What is its solubility in water at 1.5 atm and 20.0 °C?

13.45 At 740 torr and 20.0 °C, nitrogen has a solubility in water of 0.018 g L^{-1}. At 620 torr and 20.0 °C, its solubility is 0.015 g L^{-1}. Show that nitrogen obeys Henry's law.

13.46 If the solubility of a gas in water is 0.010 g L^{-1} at 25 °C with the partial pressure of the gas over the solution at 1.0 atm, predict the solubility of the gas at the same temperature but at double the pressure.

13.47 If 100.0 mL of water is shaken with oxygen gas at 1.0 atm it will dissolve 0.0039 g O_2. Estimate the Henry's law constant for oxygen gas in water.

Expressions of Concentration

***13.48** What is the molality of NaCl in a solution that is 3.000 *M* NaCl, with a density of 1.07 g mL^{-1}?

***13.49** A solution of acetic acid, CH_3COOH, has a concentration of 0.143 *M* and a density of 1.00 g mL^{-1}. What is the molality of this solution?

13.50 What is the molal concentration of glucose, $C_6H_{12}O_6$, a sugar found in many fruits, in a solution made by dissolving 24.0 g of glucose in 1.00 kg of water? What is the mole fraction of glucose in the solution? What is the mass percent of glucose in the solution?

13.51 If you dissolved 11.5 g of NaCl in 1.00 kg of water, what would be its molal concentration? What are the mass percent NaCl and the mole percent NaCl in the solution? The volume of this solution is virtually identical to the original volume of the 1.00 kg of water. What is the molar concentration of NaCl in this solution? What would have to be true about any solvent for one of its dilute solutions to have essentially the same molar and molal concentrations?

13.52 A solution of ethanol, CH_3CH_2OH, in water has a concentration of 1.25 *m*. Calculate the mass percent of ethanol.

13.53 A solution of NaCl in water has a concentration of 19.5%. Calculate the molality of the solution.

OH **13.54** A solution of NH_3 in water has a concentration of 7.50% by mass. Calculate the mole percent NH_3 in the solution. What is the molal concentration of the NH_3?

13.55 An aqueous solution of isopropyl alcohol, C_3H_8O, rubbing alcohol, has a mole fraction of alcohol equal to 0.250. What is the percent by mass of alcohol in the solution? What is the molality of the alcohol?

ILW **13.56** Sodium nitrate, $NaNO_3$, is sometimes added to tobacco to improve its burning characteristics. An aqueous solution of $NaNO_3$ has a concentration of 0.363 *m*. Its density is 1.0185 g mL^{-1}. Calculate the molar concentration of $NaNO_3$ and the mass percent of $NaNO_3$ in the solution. What is the mole fraction of $NaNO_3$ in the solution?

13.57 In an aqueous solution of sulfuric acid, the concentration is 1.89 mol% of acid. The density of the solution is 1.0645 g mL^{-1}. Calculate the following: **(a)** the molal concentration of H_2SO_4, **(b)** the mass percent of the acid, and **(c)** the molarity of the solution.

Raoult's Law

OH **13.58** At 25 °C, the vapor pressure of water is 23.8 torr. What is the vapor pressure of a solution prepared by dissolving 65.0 g of $C_6H_{12}O_6$ (a nonvolatile solute) in 150 g of water? (Assume the solution is ideal.)

13.59 The vapor pressure of water at 20 °C is 17.5 torr. A 35% solution of the nonvolatile solute ethylene glycol, $C_2H_4(OH)_2$, in water is prepared. Estimate the vapor pressure of the solution.

13.60 At 25 °C the vapor pressures of benzene (C_6H_6) and toluene (C_7H_8) are 93.4 and 26.9 torr, respectively. A solution made by mixing 35.0 g of benzene and 65.0 g of toluene is prepared. At what applied pressure, in torr, will this solution boil?

13.61 Pentane (C_5H_{12}) and heptane (C_7H_{16}) are two hydrocarbon liquids present in gasoline. At 20.0 °C, the vapor pressure of pentane is 422 torr and the vapor pressure of heptane is 36.0 torr. What will be the total vapor pressure (in torr) of a solution prepared by mixing equal masses of the two liquids?

***13.62** Benzene and toluene help achieve good engine performance from lead-free gasoline. At 40 °C, the vapor pressure of benzene is 184 torr and that of toluene is 58 torr. Suppose you wished to prepare a solution of these liquids that will have a total vapor pressure of 96 torr at 40 °C. What must be the mole percent concentrations of each in the solution?

***13.63** The vapor pressure of pure methanol, CH_3OH, at 33 °C is 164 torr. How many grams of the nonvolatile solute glycerol, $C_3H_5(OH)_3$, must be added to 105 g of methanol to obtain a solution with a vapor pressure of 145 torr?

***13.64** A solution containing 8.3 g of a nonvolatile, nondissociating substance dissolved in 1.00 mol of chloroform, $CHCl_3$, has a vapor pressure of 511 torr. The vapor pressure of pure $CHCl_3$ at the same temperature is 526 torr. Calculate **(a)** the mole fraction of the solute, **(b)** the number of moles of solute in the solution, and **(c)** the molecular mass of the solute.

***13.65** At 21.0 °C, a solution of 18.26 g of a nonvolatile, nonpolar compound in 33.25 g of ethyl bromide, C_2H_5Br, had a vapor pressure of 336.0 torr. The vapor pressure of pure ethyl bromide at this temperature is 400.0 torr. Assuming an ideal solution, what is the molecular mass of the compound?

Freezing Point Depression and Boiling Point Elevation

13.66 How many grams of sucrose ($C_{12}H_{22}O_{11}$) are needed to lower the freezing point of 125 g of water by 3.00 °C?

13.67 To make sugar candy, a concentrated sucrose solution is boiled until the temperature reaches 272 °F. What are the molality and the mole fraction of sucrose in this mixture?

13.68 A solution of 14 g of a nonvolatile, nondissociating compound in 0.10 kg of benzene boils at 81.7 °C. Calculate the molecular mass of the unknown.

OH **13.69** A solution of 12.00 g of an unknown nondissociating compound dissolved in 200.0 g of benzene freezes at 3.45 °C. Calculate the molecular mass of the unknown.

ILW ***13.70** What are the molecular mass and molecular formula of a nondissociating molecular compound whose empirical formula is C_4H_2N if 3.84 g of the compound in 0.500 kg of benzene gives a freezing point depression of 0.307 °C?

***13.71** Benzene reacts with hot concentrated nitric acid dissolved in sulfuric acid to give chiefly nitrobenzene, $C_6H_5NO_2$. A by-product is often obtained, which consists of 42.86% C, 2.40% H, and 16.67% N (by mass). The boiling point of a solution of 5.5 g of the by-product in 45 g of benzene was 1.84 °C higher than that of benzene. **(a)** Calculate the empirical formula of the by-product. **(b)** Calculate a molecular mass of the by-product and determine its molecular formula.

Osmotic Pressure

ILW **13.72** **(a)** Show that the following equation is true.

$$\text{Molar mass of solute} = \frac{(\text{grams of solute})RT}{\Pi V}$$

(b) An aqueous solution of a compound with a very high molecular mass was prepared in a concentration of 2.0 g L^{-1} at 25 °C. Its osmotic pressure was 0.021 torr. Calculate the molecular mass of the compound.

OH **13.73** A saturated solution is made by dissolving 0.400 g of a polypeptide (a substance formed by joining together in a chainlike fashion a number of amino acids) in water to give 1.00 L of solution. The solution has an osmotic pressure of 3.74 torr at 27 °C. What is the approximate molecular mass of the polypeptide?

Colligative Properties of Electrolyte Solutions

13.74 The vapor pressure of water at 20.0 °C is 17.5 torr. At that temperature, what would be the vapor pressure of a solution made by dissolving 23.0 g of NaCl in 0.100 kg of water? (Assume complete dissociation of the solute and an ideal solution.)

13.75 How many grams of $AlCl_3$ would have to be dissolved in 0.150 L of water to give a solution that has a vapor pressure of 38.7 torr at 35 °C? Assume complete dissociation of the solute and ideal solution behavior. (At 35 °C, the vapor pressure of pure water is 42.2 torr.)

OH **13.76** What is the osmotic pressure, in torr, of a 2.0% solution of NaCl in water when the temperature of the solution is 25 °C?

13.77 Below are the concentrations of the most abundant ions in seawater.

Ion	Molality
Chloride	0.566
Sodium	0.486
Magnesium	0.055
Sulfate	0.029
Calcium	0.011
Potassium	0.011
Bicarbonate	0.002

Use these data to estimate the osmotic pressure of seawater at 25 °C in units of atm. What is the minimum pressure in atm needed to desalinate seawater by reverse osmosis?

13.78 What is the expected freezing point of a 0.20 *m* solution of $CaCl_2$? (Assume complete dissociation.)

13.79 The freezing point of a 0.10 *m* solution of mercury(I) nitrate is approximately −0.27 °C. Show that these data suggest that the formula of the mercury(I) ion is Hg_2^{2+}.

Interionic Attractions and Colligative Properties

13.80 The van't Hoff factor for the solute in 0.100 *m* $NiSO_4$ is 1.19. What would this factor be if the solution behaved as if it were 100% dissociated?

13.81 What is the expected van't Hoff factor for K_2SO_4 in an aqueous solution, assuming 100% dissociation?

13.82 A 0.118 *m* solution of LiCl has a freezing point of −0.415 °C. What is the van't Hoff factor for this solute at this concentration?

13.83 What is the approximate osmotic pressure of a 0.118 *m* solution of LiCl at 10 °C? Express the answer in torr. (Use the data in Problem 13.82.)

Additional Problems

***13.84** The "bends" is a medical emergency caused by the formation of tiny bubbles in the blood vessels of divers who rise too quickly to the surface from a deep dive. The origin of the problem is seen in the calculations in this problem. At 37 °C (normal body temperature), the solubility of N_2 in water is 0.015 g L^{-1} when its pressure over the solution is 1 atm. Air is approximately 78 mol% N_2. How many moles of N_2 are dissolved per liter of blood (essentially an aqueous solution) when a diver inhales air at a pressure of 1 atm? How many moles of N_2 dissolve per liter of blood when the diver is submerged to a depth of approximately 100 ft, where the total pressure of the air being breathed is 4 atm? If the diver suddenly surfaces, how many milliliters of N_2 gas, in the form of tiny bubbles, are released into the bloodstream from each liter of blood (at 37 °C and 1 atm)?

OH **13.85** The vapor pressure of a mixture of 0.400 kg of carbon tetrachloride and 43.3 g of an unknown compound is 137 torr at 30 °C. At the same temperature, the vapor pressure of pure carbon tetrachloride is 143 torr, while that of the pure unknown is 85 torr. What is the approximate molecular mass of the unknown? Will our estimate of the molecular mass be too high or too low if the heat of solution is exothermic?

OH **13.86** What is the osmotic pressure in torr of a 0.010 *M* aqueous solution of a molecular compound at 25 °C?

***13.87** Ethylene glycol, $C_2H_6O_2$, is used in many antifreeze mixtures. Protection against freezing to as low as −45 °F is sought.

(a) How many moles of solute are needed per kilogram of water to ensure this protection?

(b) The density of ethylene glycol is 1.11 g mL^{-1}. To how many milliliters of solute does your answer to part **(a)** correspond?

(c) Calculate the number of quarts of ethylene glycol that should be mixed with each quart of water to get the desired protection.

***13.88** The osmotic pressure of a dilute solution of a slightly soluble *polymer* (a compound composed of large molecules formed by linking many smaller molecules together) in water was measured using the osmometer in Figure 13.21. The difference in the heights of the liquid levels was determined to be 1.26 cm at 25 °C. Assume the solution has a density of 1.00 g mL^{-1}. **(a)** What is the osmotic pressure of the solution in torr? **(b)** What is the molarity of the solution? **(c)** At what temperature would the solution be expected to freeze? **(d)** On the basis of the results of these calculations, explain why freezing point depression cannot be used to determine the molecular masses of compounds composed of very large molecules.

13.89 A solution of ethanol, C_2H_5OH, in water has a concentration of 4.613 mol L^{-1}. At 20.0 °C, its density is 0.9677 g mL^{-1}. Calculate the following: **(a)** the molality of the solution and **(b)** the mass percentage of the alcohol in the mixture.

13.90 Consider an aqueous 1.00 *m* solution of Na_3PO_4, a compound with useful detergent properties.

(a) Calculate the boiling point of the solution on the assumption that it does not ionize at all in solution.

(b) Do the same calculation, assuming that the van't Hoff factor for Na_3PO_4 reflects 100% dissociation into its ions.

(c) The 1.00 *m* solution boils at 100.183 °C at 1 atm. Calculate the van't Hoff factor for the solute in this solution.

***13.91** A 2.50 g sample of aluminum chloride and sodium sulfate has a freezing point depression of 2.65 °C. Assuming complete dissociation of all ions, what are the molarities of aluminum chloride and sodium sulfate?

Multi-Concept Problems

***13.92** A sample containing only iron(II) nitrate and potassium chloride is dissolved in water and the boiling point of the mixture is 104.6 °C. That same solution is reacted with 36.3 mL of 0.220 *M* $K_2Cr_2O_7$ solution that completely converts the iron(II) to iron(III). What are the molarities of iron(II) nitrate and potassium chloride in the original solution? The density of the mixture is 1.032 g/mL and we assume all soluble species are completely dissociated.

***13.93** A 25.00 mL sample of a 0.200 *M* solution of barium nitrate is mixed with 14.00 mL of a 0.250 *M* solution of potassium sulfate. Assuming that all ionic species are completely dissociated, what is the osmotic pressure of the mixture in torr?

***13.94** A compound is found to have a molecular formula of C_2H_6O. Write all of the possible structural formulas for this compound. With a relevant explanation, determine whether each of your structures will

(a) be expected to be a solid, liquid or gas at 25 °C.

(b) be soluble in water or pentane.

(c) form hydrogen bonds.

(d) be a strong electrolyte, a weak electrolyte, or a nonelectrolyte.

***13.95** How many mL of 0.223 *M* $K_2Cr_2O_7$ are needed to completely oxidize 155 mL of 0.650 *M* tin(II) chloride to tin(IV)? When the reaction is complete, what will the osmotic pressure be, in torr?

***13.96** An experiment calls for the use of the dichromate ion, $Cr_2O_7^{2-}$, in sulfuric acid as an oxidizing agent for isopropyl alcohol, C_3H_8O. The chief product is acetone, C_3H_6O, which forms according to the following equation.

$$3C_3H_8O + Na_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3C_3H_6O + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

(a) The oxidizing agent is available only as sodium dichromate dihydrate. What is the minimum number of grams of sodium dichromate dihydrate needed to oxidize 21.4 g of isopropyl alcohol according to the balanced equation?

(b) The amount of acetone actually isolated was 12.4 g. Calculate the percentage yield of acetone.

(c) The reaction produces a volatile by-product. When a sample of it with a mass of 8.654 mg was burned in oxygen, it was converted into 22.368 mg of carbon dioxide and 10.655 mg of water, the sole products. (Assume that any unaccounted for element is oxygen.) Calculate the percentage composition of the by-product and determine its empirical formula.

(d) A solution prepared by dissolving 1.338 g of the by-product in 115.0 g of benzene had a freezing point of 4.87 °C. Calculate the molecular mass of the by-product and write its molecular formula.

Exercises in Critical Thinking

13.97 A certain organic substance is soluble in solvent *A* but it is insoluble in solvent *B*. If solvents *A* and *B* are miscible, will the organic compound be soluble in a mixture of *A* and *B*? What additional information is needed to answer this question?

13.98 The situation described in Problem 13.97 is actually quite common. How might it be used to purify the organic compound?

13.99 Compile and review all of the methods discussed for the determination of molecular masses. Assess which methods are the most reliable, most sensitive, and which are the most convenient to use.

13.100 Having had some laboratory experience by now, evaluate whether preparation of a 0.25 *molar* solution is easier or more difficult than preparing a 0.25 *molal* solution. What experiments require the use of *molal* concentrations?

13.101 This chapter focused on the physical description of osmosis and its use in determining molar masses. What other uses are there for osmosis?

13.102 Using the principles developed in this chapter, explain why all solids will eventually result in a saturated solution if enough solid is added to the solvent.

13.103 It is observed that when 10.0 g of a substance is dissolved in a specific solvent, 2.43 kJ of heat are produced. When the next 10.0 gram sample is added and dissolved, 2.16 kJ of heat are produced. Use the concepts of state functions and the principles in Section 13.2 to explain this observation.

13.104 What would be the result if molarity rather than molality was used in freezing point depression (and boiling point elevation) experiments? What changes would be needed to make the molarity system work?

Chapters 11–13

[Bringing It Together]

Again we pause to provide you with an opportunity to see how well you have grasped concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–10. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. A 9.46 g sample of neon at 25.0 °C and a pressure of 748 torr is kept at 25.0 °C as it is allowed to expand to a final volume of 25.4 L. What is the final pressure?

2. An 8.95 L sample of nitrogen at 25.0 °C and 1.00 atm is compressed to a volume of 0.895 L and a pressure of 5.56 atm. What must its final temperature be?

3. What is the chemical symbol of a gaseous element if 6.45 g of it occupies 1.92 L at 745 torr and 25.0 °C?

4. What is the molar mass of a gaseous element if at room temperature it effuses through a pinhole 2.16 times as rapidly as xenon? Which element is it?

5. If a gas in a cylinder pushes back a piston against a constant opposing pressure of 3.0×10^5 pascals and undergoes a volume change of 0.50 m^3, how much work will the gas do, expressed in joules?

6. A sample of oxygen-enriched air with a volume of 12.5 L at 25.0 °C and 1.00 atm consists of 45.0% (v/v) oxygen and 55.0% (v/v) nitrogen. What are the partial pressures of oxygen and nitrogen (in torr) in this sample after it has been warmed to a temperature of 37.0 °C and its volume is changed to 10.7 L?

7. How many milliliters of dry CO_2, measured at STP, could be evolved in the reaction between 20.0 mL of 0.100 *M* $NaHCO_3$ and 30.0 mL of 0.0800 *M* HCl?

8. How many milliliters of Cl_2 gas, measured at 25 °C and 740 torr, are needed to react with 10.0 mL of 0.10 *M* NaI if the I^- is oxidized to IO_3^- and Cl_2 is reduced to Cl^-?

9. Potassium hypobromite converts ammonia to nitrogen by a reaction in which hypobromite ion is reduced to bromide ion. To prepare 475 mL of dry N_2, when measured at 24.0 °C and 738 torr, what is the minimum number of grams of potassium hypobromite required?

10. Hydrogen peroxide, H_2O_2, is decomposed by potassium permanganate according to the following reaction.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5O_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

What is the minimum number of milliliters of 0.125 *M* $KMnO_4$ required to prepare 375 mL of dry O_2 when the gas volume is measured at 22.0 °C and 738 torr?

11. A sample of 248 mL of wet nitrogen gas was collected over water at a total gas pressure of 736 torr and a temperature of 21.0 °C. (The vapor pressure of water at 21.0 °C is 18.7 torr.) The nitrogen was produced by the reaction of sulfamic acid, HNH_2SO_3, with 425 mL of a solution of sodium nitrite according to the following equation.

$$NaNO_2 + HNH_2SO_3 \longrightarrow N_2 + NaHSO_4 + H_2O$$

Calculate what must have been the molar concentration of the sodium nitrite.

12. One way to make chlorine gas is to let manganese(IV) oxide react with hydrochloric acid in which the manganese is reduced to Mn^{2+}. What is the minimum volume (in mL) of 6.44 *M* HCl needed to prepare 525 mL of dry chlorine when the gas is obtained at 24.0 °C and 742 torr?

13. Hexanitroethane, $C_2(NO_2)_6$, decomposes explosively if heated above 140 °C. It is estimated that ΔH_f° for $C_2(NO_2)_6(s)$ is +96 kJ mol^{-1}. (a) Calculate ΔH° for the decomposition of $C_2(NO_2)_6$ according to the equation

$$C_2(NO_2)_6(s) \longrightarrow 2NO_2(g) + 4NO(g) + 2CO_2(g)$$

(b) Suppose 1.26 g of $C_2(NO_2)_6(s)$ is placed in a 200.0 cm^3 vessel where it is detonated. The heat capacities, C_v, at 25 °C for the gases formed are as follows: CO_2, 28.5 J mol^{-1} K^{-1}; NO, 21.5 J mol^{-1} K^{-1}; NO_2, 29.5 J mol^{-1} K^{-1}. Assuming the heat capacities don't change and all the heat liberated in the reaction remains in the container, what will be the pressure of the mixture of gases after detonation?

14. Consider the molecule $POCl_3$, in which phosphorus is the central atom and is bonded to an oxygen atom and three chlorine atoms.

(a) Draw the Lewis structure of $POCl_3$ and predict its geometry.

(b) Is the molecule polar or nonpolar? Explain.

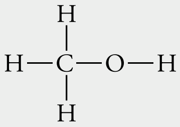
(c) What kinds of attractive forces would be present between $POCl_3$ molecules in the liquid?

15. What kinds of attractive forces, including chemical bonds, would be present between the particles in

(a) $H_2O(l)$
(b) $CCl_4(l)$
(c) $CH_3OH(l)$
(d) $BrCl(l)$
(e) $NaCl(s)$
(f) $Na_2SO_4(s)$

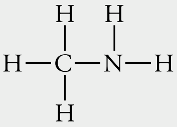
16. Trimethylamine $(CH_3)_3N$, is a substance responsible in part for the smell of fish. It has a boiling point of 3.5 °C and a molecular weight of 59.1. Dimethylamine, $(CH_3)_2NH$, has a similar odor and boils at a slightly higher temperature, 7 °C, even though it has a somewhat lower molecular mass (45.1). How can this be explained in terms of the kinds of attractive forces between their molecules?

17. Methanol, CH_3OH, commonly known as wood alcohol, has a boiling point of 64.7 °C. Methylamine, a fishy-smelling chemical found in herring brine, has a boiling point of −6.3 °C. Ethane, a hydrocarbon present in petroleum, has a boiling point of −88 °C.



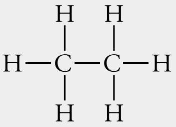
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & O-H \\ & & | & & \\ & & H & & \end{array}$$

methanol
b.p. 64.7 °C



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & N & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

methylamine
b.p. −6.3 °C



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethane
b.p. −88 °C

Each has nearly the same molecular mass. Account for the large differences in their boiling points in terms of the attractive forces between their molecules.

18. Based on what you've learned in these chapters, explain:

(a) Why a breeze cools you when you're perspiring.

(b) Why droplets of water form on the outside of a glass of cold soda on a warm, humid day.

(c) Why you feel more uncomfortable on a warm, humid day than on a warm, dry day.

(d) The origin of the energy in a violent thunderstorm.

(e) Why clouds form as warm, moist air flows over a mountain range.

19. Aluminum has a density of 2.70 g cm^{-3} and crystallizes in a face-centered cubic lattice. Use these and other data to calculate the atomic radius of an aluminum atom.

20. What is the difference between the closest-packed structures identified as ccp and hcp? In each of these structures, how many atoms are in contact with any given atom?

21. Tin tetraiodide [tin(IV) iodide] has the formula SnI_4. It forms soft, yellow to reddish crystals that melt at about 143 °C. What kind of solid does SnI_4 form? What kind of bonding occurs in SnI_4?

22. Sketch the phase diagram for a substance that has a triple point at 25 °C and 100 torr, a normal boiling point of 150 °C, and a melting point at 1 atm of 27 °C. Is the solid more dense or less dense than the liquid? Where on the curve would the critical temperature and critical pressure be? What phase would exist at 30 °C and 10.0 torr?

23. How many grams of 4.00% (w/w) solution of KOH in water are needed to neutralize completely the acid in 10.0 mL 0.256 M H_2SO_4?

24. Calculate the molar concentration of 15.00% (w/w) Na_2CO_3 solution at 20.0 °C given that its density is 1.160 g/mL.

25. The solubility of pure oxygen in water at 20.0 °C and 760 torr is 4.30×10^{-2} g O_2 per liter of H_2O. When air is in contact with water and the air pressure is 585 torr at 20 °C, how many grams of oxygen from the air dissolve in 1.00 L of water? The average concentration of oxygen in the air is 21.1% (v/v).

26. If the element gallium, Ga, is added to germanium, which kind of semiconductor (*n* or *p*) will result? Explain your answer.

27. Compound XY is an ionic compound that dissociates as it dissolves in water. The lattice energy of XY is −600 kJ/mol. The hydration energy of its ions is −610 kJ/mol.

(a) Write the thermochemical equations for the two steps in the formation of a solution of XY in water.

(b) Write the sum of these two equations in the form of a thermochemical equation, showing the net ΔH.

(c) Draw an enthalpy diagram for the formation of this solution.

28. At 20 °C a 40.00% (v/v) solution of ethanol in water has a density of 0.9369 g/mL. (Such a solution could be prepared, for example, by mixing 40.00 mL of ethanol with enough water to give 100.00 mL of solution.) The density of pure ethanol at this temperature is 0.7907 g/mL and that of water is 0.9982 g/mL.

(a) Calculate the molar concentration and the molal concentration of ethanol in this solution.

(b) Calculate the concentration of ethanol in this solution in mole fractions and mole percents.

(c) The vapor pressure of ethanol at 20 °C is 41.0 torr and of water is 17.5 torr. If the 40.00% (v/v) solution were ideal, what would be the vapor pressure of each component over the solution?

29. Estimate the boiling point of 1.0 molal $Al(NO_3)_3$, assuming that it dissociates entirely into Al^{3+} and NO_3^- ions in solution.

30. Squalene is an oil found chiefly in shark liver oil but is also present in low concentrations in olive oil, wheat germ oil, and yeast. A qualitative analysis disclosed that its molecules consist entirely of carbon and hydrogen. When a sample of squalene with a mass of 0.5680 g was burned in pure oxygen, there was obtained 1.8260 g of carbon dioxide and 0.6230 g of water.

(a) Calculate the empirical formula of squalene.

(b) When 0.1268 g of squalene was dissolved in 10.50 g of molten camphor, the freezing point of this solution was 177.3 °C. (The melting point of pure camphor is 178.4 °C, and its molal freezing point depression constant is 37.5 °C kg $camphor^{-1}$.) Calculate the formula mass of squalene and determine its molecular formula.

14 Chemical Kinetics

Chapter Outline

14.1 | Factors that Affect Reaction Rates

14.2 | Measuring Reaction Rates

14.3 | Rate Laws

14.4 | Integrated Rate Laws

14.5 | Molecular Basis of Collision Theory

14.6 | Molecular Basis of Transition State Theory

14.7 | Activation Energies

14.8 | Mechanisms of Reactions

14.9 | Catalysts

Why can't butterflies fly when it is cold? When the temperature drops, insects move slower because the chemical reactions that allow their muscles to move occur at slower rates. As we will see in this chapter, the rates of reactions depend on the temperatures at which they occur. The butterfly was too cold, so the reactions needed to contract the muscles were too slow to allow the butterfly to fly away. Courtesy of James Brady

This Chapter in Context

Chemical reactions run at many different speeds. Some, such as the rusting of iron or the breakdown of plastics in the environment, take place very slowly. Others, like the combustion of gasoline or the explosion of gunpowder, occur very quickly. **Chemical kinetics** is the study of the speeds (or *rates*) of chemical reactions. On a practical level, chemical kinetics is concerned with factors that affect the speeds of reactions and how reaction speeds can be controlled. This is essential in industry, where synthetic reactions must take place at controlled speeds. If a reaction takes weeks or months to occur, it may not be economically feasible; if it occurs too quickly or uncontrollably, it may result in an explosion. For the consumer, studies on rates of decomposition allow a manufacturer to reliably determine the shelf life, or expiration date, of a product or drug. At a more fundamental level, a study of the speed of a reaction often gives clues that lead to an understanding about *how*, at the molecular level, reactants change into products. Understanding the reaction at this level of detail often allows more precise control of the reaction's speed, and suggests ways to modify the reaction to produce new types of products, or to improve the reaction's yield by preventing undesirable side reactions from occurring.

14.1 | Factors that Affect Reaction Rates

The **rate of reaction** for a given chemical change is the speed with which the reactants disappear and the products form. When a reaction is fast, more product is formed in a given period of time than in a slow reaction. Reaction rate is measured by the amount of products produced or reactants consumed per unit time. Usually this is done by monitoring the concentrations of the reactants or products over time, as the reaction proceeds (see Figure 14.1).

Before we take up the quantitative aspects of reaction rates, let's look qualitatively at factors that can make a reaction run faster or slower. There are five principal factors that influence reaction rates.

1. Chemical nature of the reactants themselves
2. Ability of the reactants to come in contact with each other
3. Concentrations of the reactants
4. Temperature
5. Availability of rate-accelerating agents called *catalysts*

TOOLS

Factors that affect reaction rates

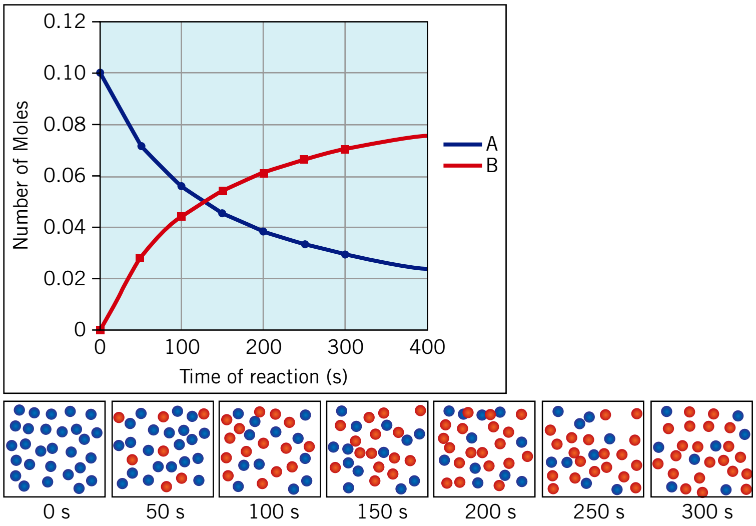


Figure 14.1 | **Reaction rates are measured by monitoring concentration changes over time.** For the reaction, $A \longrightarrow B$, the number of A molecules (in blue) decreases with time as the number of B molecules (in red) increases. The steeper the concentration versus time curves are, the faster the rate of reaction is. The filmstrip represents the relative numbers of molecules of A and B at each time.

Chemical Nature of the Reactants

Bonds break and new bonds form during reactions. The most fundamental differences among reaction rates, therefore, lie in the reactants themselves, in the inherent tendencies for their atoms, molecules, or ions to undergo changes in chemical bonds or oxidation states. Some reactions are fast by nature and others are slow (Figure 14.2). For example, because sodium atoms lose electrons easily, a freshly exposed surface of metallic sodium tarnishes when exposed to air and moisture. Under identical conditions, potassium also reacts with air and moisture, but the reaction is much faster because potassium atoms lose electrons more easily than sodium atoms.

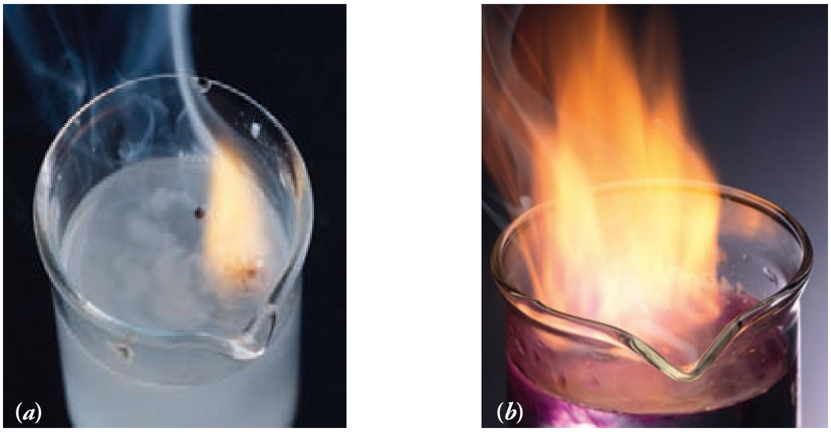


Figure 14.2 | **The chemical nature of reactants affects reaction rates.** (*a*) Sodium loses electrons easily, so it reacts quickly with water. (*b*) Potassium loses electrons even more easily than sodium, so its reaction with water is explosively fast. *(Fundamental Photographs)*

Ability of the Reactants to Meet

Most reactions involve two or more reactants whose particles (i.e., atoms, ions, or molecules) must collide with each other for the reaction to occur. This is why reactions are often carried out in liquid solutions or in the gas phase. In these states, the particles are able to intermingle at a molecular level and collide with each other easily.

Reactions in which all of the reactants are in the same phase are called **homogeneous reactions.** Examples include the neutralization of sodium hydroxide by hydrochloric acid when both are dissolved in water, and the explosive reaction in the gas phase of gasoline vapor with oxygen that can occur when the two are mixed in the right proportions in a gasoline engine. (An *explosion* is an extremely rapid reaction that generates hot expanding gases.)

When the reactants are present in different phases—for example, when one is a gas and the other is a liquid or a solid—the reaction is called a **heterogeneous reaction**. In a heterogeneous reaction, the reactants are able to meet only at the interface between the phases, so *the area of contact between the phases is a major factor in determining the rate of the reaction.* This area is controlled by the sizes of the particles of the reactants. By pulverizing a solid, the total surface area can be hugely increased (Figure 14.3). This maximizes contact between the atoms, ions, or molecules in the solid state with those in a different phase. As a result, in heterogeneous reactions, smaller particles tend to react faster than large ones.

Although heterogeneous reactions such as those just illustrated are important, they are very complex and difficult to analyze. In this chapter, therefore, we'll focus mostly on homogeneous systems.

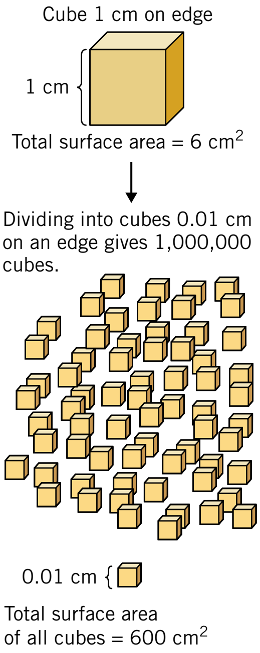

Cube 1 cm on edge
1 cm
Total surface area = 6 cm²
Dividing into cubes 0.01 cm on an edge gives 1,000,000 cubes.
0.01 cm
Total surface area of all cubes = 600 cm²

Figure 14.3 | **Effect of crushing a solid.** When a single solid is subdivided into much smaller pieces, the total surface area on all of the pieces becomes very large.

Concentrations of the Reactants

The rates of both homogeneous and heterogeneous reactions are affected by the concentrations of the reactants. For example, wood burns relatively quickly in air but extremely rapidly in pure oxygen. It has been estimated that if air were 30% oxygen instead of 21%, it would be impossible to put out forest fires. Even red hot steel wool, which only sputters and glows in air, bursts into flame when thrust into pure oxygen (see Figure 14.4).

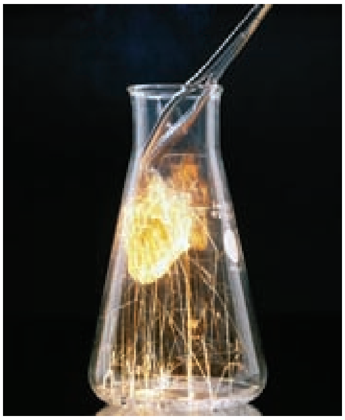


Figure 14.4 | **Effect of concentration on rate.** Using pure oxygen instead of air, steel wool, after being heated to redness in a flame, burns spectacularly. *(© 1993 Richard Megna/ Fundamental Photographs)*

Temperature of the System

Chemical reactions occur faster at higher temperatures than they do at lower temperatures. You may have noticed, for example, that insects move more slowly when the air is cool, as in the chapter-opening photograph of the butterfly. An insect is a cold-blooded creature, which means that its body temperature is determined by the temperature of its surroundings. As the air cools, insects cool, and so the rates of their metabolic reactions slow down, making the insects sluggish.

Presence of Catalysts

Catalysts are substances that increase the rates of chemical reactions without being used up. They affect every moment of our lives. In our bodies, substances called enzymes serve as catalysts for biochemical reactions. By making enzymes available or not, a cell is able to direct our body chemistry by controlling which chemical reactions can occur rapidly. Catalysts are used in the chemical industry to make gasoline, plastics, fertilizers, and other products that have become virtual necessities in our lives.

14.2 | Measuring Reaction Rates

The qualitative factors discussed in Section 14.1 can also be described quantitatively. To do this, we need to express reaction rates in mathematical terms. Let's start with the concept of **rate**, a change in quantity per unit time. This always implies a ratio in which a unit of time is in the denominator. Suppose, for example, that you have a job with a pay rate of ten dollars per hour. Because *per* can be translated as *divided by*, your rate of pay can be written as a fraction (abbreviating hour as hr):

$$\text{Rate of pay} = 10 \text{ dollars per hour} = \frac{10 \text{ dollars}}{1 \text{ hr}} = 10 \text{ dollars hr}^{-1}$$

Here we've expressed the fraction 1/hr as hr^{-1}.

When chemical reactions occur, the concentrations of reactants decrease as they are used up, while the concentrations of the products increase as they form. So, one way to describe a reaction's rate is to pick one substance in the reaction's equation and describe its change in concentration per unit of time. The result is the rate of the reaction *with respect to that substance.* Remembering that we always take "final minus initial," the rate of reaction with respect to substance X is given in Equation 14.1.

$$\begin{aligned}\text{Rate with respect to } X &= \frac{(\text{conc. of } X \text{ at time } t_\text{f} - \text{conc. of } X \text{ at time } t_\text{i})}{(t_\text{f} - t_\text{i})} \\ &= \frac{\Delta(\text{conc. of } X)}{\Delta t} \qquad (14.1)\end{aligned}$$

TOOLS

Rate with respect to one reactant or product

Molarity (mol/L) is normally the concentration unit, and the second (s) is the most often used unit of time. Therefore, the units for reaction rates are most frequently the following:

$$\frac{\text{mol/L}}{\text{s}}$$

The units for a reaction rate can also be expressed as **mol L⁻¹ s⁻¹**. By convention, reaction rate is reported as a positive value, whether the rate was measured as the concentration of the product increases or the concentration of the reactants decreases. For instance, if the concentration of one product of a reaction increases by 0.50 mol/L each second, the rate of its formation is 0.50 mol L^{-1} s^{-1}. Similarly, if the concentration of a reactant decreases by 0.20 mol/L per second, its rate with respect to the reactant is 0.20 mol L^{-1} s^{-1}.

Relative Rates and Reaction Stoichiometry

When we know the value of a reaction rate with respect to one substance, the coefficients of the reaction's balanced chemical equation can be used to find the rates with respect to the other substances. For example, in the combustion of propane,

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

five moles of O_2 *must* be consumed per unit of time for each mole of C_3H_8 used in the same time. In this reaction, therefore, oxygen *must* react five times faster than propane in units of mol L^{-1} s^{-1}. Similarly, CO_2 forms three times faster than C_3H_8 reacts and H_2O forms four times faster. The magnitudes of the rates relative to each other are thus in the same relationship as the coefficients in the balanced chemical equation.

Example 14.1
Relationships of Rates within a Reaction

Butane, the fuel in cigarette lighters, burns in oxygen to give carbon dioxide and water. If, in a certain experiment, the butane concentration is decreasing at a rate of 0.20 mol L^{-1} s^{-1}, what is the rate at which the oxygen concentration is decreasing, and what are the rates at which the product concentrations are increasing?

■ **Analysis:** As always, we need a balanced chemical equation. Butane, C_4H_{10}, burns in oxygen to give CO_2 and H_2O according to the following balanced chemical equation:

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

We now need to relate the rate with respect to oxygen and the products to the given rate with respect to butane. The magnitudes of the rates relative to each other are in the same relationship as the coefficients in the balanced chemical equation.

■ **Assembling the Tools:** The chemical equation is the tool that links the stoichiometric amounts of these substances to the amount of butane. The other tool will be Equation 14.1 for calculating the rate of a reaction.

■ **Solution:** For oxygen,

$$\frac{0.20\ \cancel{\text{mol } C_4H_{10}}}{\text{L s}} \times \frac{13\ \text{mol } O_2}{2\ \cancel{\text{mol } C_4H_{10}}} = \frac{1.3\ \text{mol } O_2}{\text{L s}}$$

Oxygen is reacting at a rate of 1.3 mol L^{-1} s^{-1}. For CO_2 and H_2O, we have similar calculations:

$$\frac{0.20\ \cancel{\text{mol } C_4H_{10}}}{\text{L s}} \times \frac{8\ \text{mol } CO_2}{2\ \cancel{\text{mol } C_4H_{10}}} = \frac{0.80\ \text{mol } CO_2}{\text{L s}}$$

$$\frac{0.20\ \cancel{\text{mol } C_4H_{10}}}{\text{L s}} \times \frac{10\ \text{mol } H_2O}{2\ \cancel{\text{mol } C_4H_{10}}} = \frac{1.0\ \text{mol } H_2O}{\text{L s}}$$

Therefore,

$$\text{Rate with respect to the formation of } CO_2 = 0.80\ \text{mol L}^{-1}\ \text{s}^{-1}$$
$$\text{Rate with respect to the formation of } H_2O = 1.0\ \text{mol L}^{-1}\ \text{s}^{-1}$$

■ **Are the Answers Reasonable?** If what we've calculated is correct, then the ratio of the numerical values of the last two rates—namely, 0.80 to 1.0—should be the same as the ratio of the corresponding coefficients in the chemical equation—namely, 8 to 10 (the same ratio as 0.8 to 1.0).

Practice Exercises

14.1 | The iodate ion reacts with sulfite ions in the reaction

$$IO_3^- + 3SO_3^{2-} \longrightarrow I^- + 3SO_4^{2-}$$

At what rate are the iodide and sulfate ions being produced if the sulfite ion is disappearing at a rate of 2.4×10^{-4} mol L^{-1} s^{-1}? (*Hint:* Pay attention to the stoichiometry.)

14.2 | Hydrogen sulfide burns in oxygen to form sulfur dioxide and water. If sulfur dioxide is being formed at a rate of 0.30 mol L^{-1} s^{-1}, what are the rates of disappearance of hydrogen sulfide and oxygen?

Because the rates of reaction of reactants and products are all related, it doesn't matter which species we pick to follow concentration changes over time. For example, to study the decomposition of hydrogen iodide, HI, into H_2 and I_2,

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

it is easiest to monitor the I_2 concentration because it is the only colored substance in the reaction. As the reaction proceeds, purple iodine vapor forms, and there are instruments that allow us to relate the intensity of the color to the iodine concentration. Then, once we know the rate of formation of iodine, we also know the rate of formation of hydrogen. It is the same because the coefficients of H_2 and I_2 are the same in the balanced chemical equation. And the rate of disappearance of HI, which has a coefficient of 2 in the equation, is twice as fast as the rate of formation of I_2.

Because reactants and products are consumed and formed at different rates, we would like to find a way to express the speed of a reaction in a way that is independent of which reactant or product is monitored. To accomplish this, we divide the relative rate of reaction with respect to a given substance by the coefficient of the substance in the balanced chemical equation. The result is a quantity we will call the **rate of reaction**. Consider, for example, the combustion of propane discussed previously:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

The rate at which O_2 is changing can be expressed as

$$\text{rate } O_2 = -\frac{\Delta[O_2]}{\Delta t}$$

where we have used square brackets around the chemical formula to denote molar concentration. Because the O_2 concentration is decreasing, we need a negative sign to make the rate a positive quantity. The *rate of reaction* would then be calculated by dividing the relative rate for O_2 by its coefficient, 5.

■ Square brackets around chemical formulas is the standard way to denote molar concentration. You will see this frequently in the chapters ahead.

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}$$

Each of the other relative rates is treated in the same way to give the *same* value for the rate of reaction:

$$\text{Rate} = -\frac{1}{1}\frac{\Delta[C_3O_8]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[CO_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[H_2O]}{\Delta t}$$

For a generalized reaction

$$aA + bB \longrightarrow cC + dD$$

the rate is given by Equation 14.2,

Rate of a reaction

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{14.2}$$

Example 14.2
Rates of a Reaction

In Example 14.1, butane burned in oxygen to give carbon dioxide and water at a rate of 0.20 mol L^{-1} s^{-1} with respect to butane. What is the rate for the reaction independent of any of the reactants or products?

■ **Analysis:** We are given the rate of the reaction with respect to butane. We can use the balanced chemical equation from Example 14.1 and the stoichiometric coefficients,

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

We will relate the rate of the reaction with respect to butane to the rate of the reaction independent of the reactants or products.

■ **Assembling the Tools:** Just as in Example 14.1, we will use the balanced chemical equation as a tool because it gives the stoichiometric ratio of the reactants and products. We will then use Equation 14.2 to calculate the rate of the reaction.

■ **Solution:** We are given the relative rate of the reaction of butane as 0.20 mol L^{-1} s^{-1}. We also have the balanced chemical equation for the combustion of butane with the coefficient of 2 for butane.

$$\begin{aligned}\text{rate}_{\text{with respect to butane}} &= -\frac{\Delta[C_4H_{10}]}{\Delta t} = -\frac{0.20 \text{ mol}}{\text{L s}} \\ \text{rate}_{\text{reaction}} &= -\left[\frac{1}{2} \times \left(\frac{-0.20 \text{ mol}}{\text{L s}}\right)\right] \\ &= 0.1 \ \frac{\text{mol}}{\text{L s}}\end{aligned}$$

■ **Are the Answers Reasonable?** Since the coefficient for butane is greater than one, the rate for the reaction should be less than the rate with respect to butane. Our value, 0.1 mol L^{-1} s^{-1}, is half the value of 0.2 mol L^{-1} s^{-1}, which makes sense.

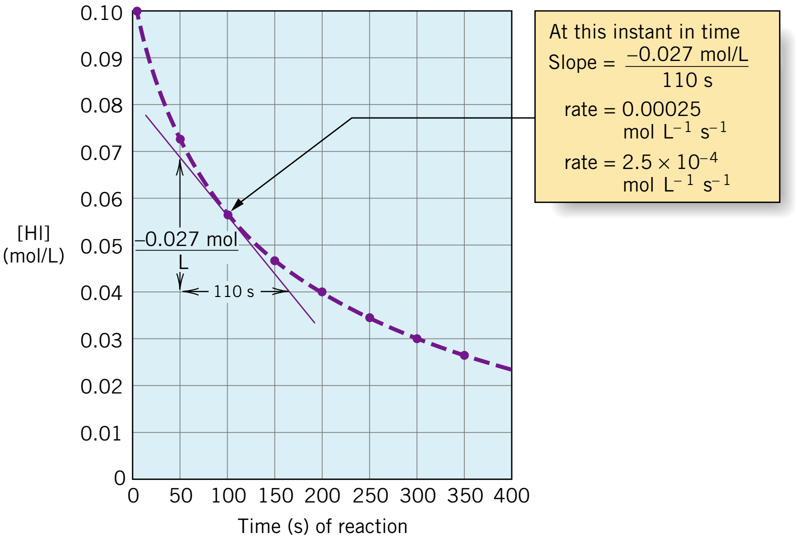
Reaction Rates versus Time

A reaction rate is rarely constant throughout the reaction but commonly changes as the reactants are used up. This is because the rate usually depends on the concentrations of the reactants, and these change as the reaction proceeds. For example, Table 14.1 lists data for the decomposition of hydrogen iodide at a temperature of 508 °C. The data, which show the changes in molar HI concentration over time, are plotted in Figure 14.5. Notice that the molar HI concentration decreases fairly rapidly during the first 50 seconds of the reaction, which means that the initial rate is relatively fast. However, later, in the interval between 300 s and 350 s, the concentration changes by only a small amount, so the rate has slowed considerably. Thus, the steepness of the curve at any moment reflects the rate of the reaction; the steeper the curve, the higher is the rate.

Table 14.1 Data, at 508 °C, for the Reaction

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

Concentration of HI (mol/L)	Time (s) (measured to 1 second)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350



At this instant in time

$\text{Slope} = \dfrac{-0.027 \text{ mol/L}}{110 \text{ s}}$

rate = 0.00025 mol L^{-1} s^{-1}

rate = 2.5×10^{-4} mol L^{-1} s^{-1}

Figure 14.5 | **Effect of time on concentration.** The data for this plot of the change in the concentration of HI with time for the reaction,

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

at 508 °C are taken from Table 14.1. The slope is negative because we're measuring the *disappearance* of HI, but when its value is used as a rate of reaction, we express the rate as positive.

The rate at which the HI is being consumed at any particular moment is called the **instantaneous rate**. When we use the term "reaction rate" we mean the instantaneous rate, unless we state otherwise. The instantaneous rate can be determined from the slope of the curve measured at the time we have chosen. The slope, which can be read off the graph, is the ratio (expressed positively) of the change in concentration to the change in time. In Figure 14.5, for example, the relative rate of the decomposition of hydrogen iodide is determined for a time 100 seconds from the start of the reaction. After the tangent to the curve is drawn, we measure a concentration change (a decrease of 0.027 mol/L) and the time change (110 s) from the graph of the tangent line. Because the rate is based on a *decreasing* concentration, we use a minus sign for the *equation* that describes this rate so that the rate itself will be a positive quantity.

■ The average rate is the slope of a line connecting two points on a concentration versus time graph. The instantaneous rate is the slope of a tangent line at a single point. The average and instantaneous rates are quite different from each other.

$$\text{Rate}_{\text{with respect to HI}} = -\left\{\frac{[\text{HI}]_{\text{final}} - [\text{HI}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}\right\} = -\left\{\frac{-0.027 \text{ mol/L}}{110 \text{ s}}\right\}$$

$$\text{Rate}_{\text{with respect to HI}} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Thus, at this moment in the reaction, the rate with respect to HI is 2.5×10^{-4} mol L^{-1} s^{-1}. In Example 14.3, we'll use this technique to obtain the *initial instantaneous rate* of the reaction—that is, the instantaneous rate of reaction at time zero.

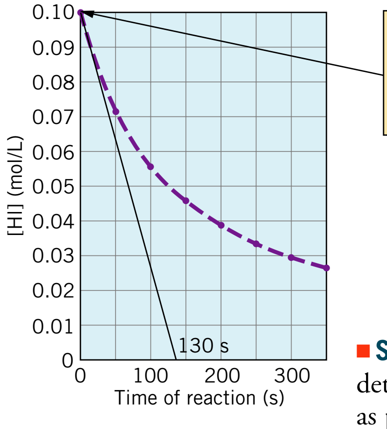
Example 14.3
Estimating the Initial Rate of a Reaction

Use the experimental data shown in Figure 14.5 for the reaction

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

to determine the initial rate of reaction at 508 °C.

■ **Analysis:** The problem asks us to determine the initial rate, which is the instantaneous rate of reaction at time zero. However, we have to be careful here to distinguish between the *rate with respect to HI* and the quantity called the *rate of reaction*, which is the rate independent of the coefficients in the balanced chemical equation. Using the slope of the tangent line at $t = 0$ will allow us to determine the instantaneous rate of reaction *with respect to HI*. To determine the *rate of reaction*, we then have to divide the rate with respect to HI by the coefficient of HI in the balanced equation.



At time zero, slope of the tangent line = –(0.10 mol/L^{-1}) / 130 s
rate = 7.7 x 10^{-4} mol L^{-1} s^{-1}

Assembling the Tools: We will find the initial rate of reaction with respect to HI by determining the slope of the tangent line at time zero of the curve showing the HI concentration as a function of time in Figure 14.5. Remember that the slope of a straight line can be calculated from the coordinates of any two points (x_1, y_1) and (x_2, y_2) using the following equation:

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1}$$

Solution: We can draw the line as shown in the graph in the margin. To more precisely determine the slope of the tangent line, we should choose two points that are as far apart as possible. The point on the curve (0 s, 0.10 mol/L) and the intersection of the tangent line with the time axis (130 s, 0 mol/L) are widely separated:

$$\text{slope} = \frac{0.10 \text{ mol/L} - 0.00 \text{ mol/L}}{0 \text{ s} - 130 \text{ s}} = -7.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

The slope is negative because the concentration of HI is decreasing as time increases. Rates are positive quantities, so we can report the initial rate of reaction with respect to HI as 7.7×10^{-4} mol L^{-1} s^{-1}.

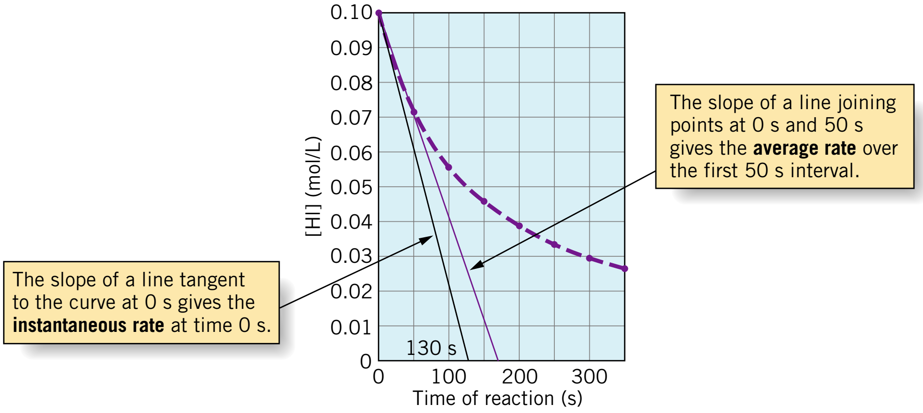
The initial rate of reaction (which is what we're asked to determine) is the rate with respect to HI divided by the coefficient of HI in the balanced equation:

$$\text{Rate of reaction} = \frac{7.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{2} = 3.9 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Is the Answer Reasonable? The instantaneous rate for HI at time zero ought to be slightly larger than the *average rate* with respect to HI between zero and 50 seconds. We can compute the average rate directly from data in Table 14.1 by selecting a pair of concentrations of HI at two different times.

$$\text{slope} = \frac{0.0716 \text{ mol/L} - 0.100 \text{ mol/L}}{50 \text{ s} - 0 \text{ s}} = -5.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Thus, the average rate from 0 to 50 s is 5.7×10^{-4} mol L^{-1} s^{-1}. As expected, this is slightly less than 7.7×10^{-4} mol L^{-1} s^{-1} the instantaneous rate with respect to HI at time zero.



The slope of a line joining points at 0 s and 50 s gives the **average rate** over the first 50 s interval.

The slope of a line tangent to the curve at 0 s gives the **instantaneous rate** at time 0 s.

Practice Exercises

14.3 | Use the graph in Figure 14.5 to estimate the rate of reaction with respect to HI at 2.00 minutes after the start of the reaction. (*Hint:* On the graph, the time is given in seconds.)

14.4 | Use the graph in Figure 14.5 to estimate the rate of reaction with respect to HI at 250 seconds after the start of the reaction.

14.3 | Rate Laws

Thus far we have focused on a rate with respect to *one* component of a reaction. This rate was the experimental rate of a process for that particular reaction. We want to broaden our focus to consider a rate expression that includes all reactants, and have an expression that can give us the rate for any set of concentrations.

Rate Laws from Reaction Rates and Concentrations

The rate of a homogeneous reaction at any instant is proportional to the product of the molar concentrations of the reactants, each molarity raised to some power or exponent that has to be found experimentally. Let's consider a chemical reaction with an equation of the following form:

$$A + B \longrightarrow \text{products}$$

Its rate of reaction can be expressed as follows:

$$\text{rate} \propto [A]^m [B]^n \tag{14.3}$$

where the values of the exponents n and m are found by experiment.

The proportionality symbol, $\propto$, in Equation 14.3 can be replaced by an equals sign if we introduce a proportionality constant, ***k***, which is called the **rate constant** for the reaction. This gives Equation 14.4:

$$\boxed{\text{rate} = k\,[A]^m [B]^n} \tag{14.4}$$

TOOLS

Rate law of a reaction

Equation 14.4 is called the **rate law** for the reaction of A with B. Once we have found values for k, n, and m, the rate law allows us to calculate the rate of the reaction at any set of known values of concentrations. Consider, for example, the following reaction.

■ The value of k depends on the particular reaction being studied, as well as the temperature at which the reaction occurs.

$$H_2SeO_3 + 6I^- + 4H^+ \longrightarrow Se + 2I_3^- + 3H_2O$$

Its rate law is of the form

$$\text{rate} = k\,[H_2SeO_3]^x [I^-]^y [H^+]^z$$

The exponents have been found experimentally to be the following for the initial rate of this reaction (i.e., the rate when the reactants are first combined).

$$x = 1, \quad y = 3, \quad \text{and} \quad z = 2$$

At 0 °C, k equals $5.0 \times 10^5\ \text{L}^5\ \text{mol}^{-5}\ \text{s}^{-1}$. (We have to specify the temperature because k varies with T.) Substituting the exponents and the value of k into the rate law equation gives the rate law for the reaction:

■ The units of the rate constant are such that the calculated rate will have the units mol $\text{L}^{-1}\ \text{s}^{-1}$.

$$\text{rate} = (5.0 \times 10^5\ \text{L}^5\ \text{mol}^{-5}\ \text{s}^{-1})\,[H_2SeO_3]\,[I^-]^3\,[H^+]^2 \qquad (\text{at } 0\ °\text{C})$$

We can calculate the initial rate of the reaction at 0 °C for any set of concentrations of H_2SeO_3, I^-, and H^+ using this rate law.

Example 14.4

Calculating Reaction Rate from the Rate Law

In the stratosphere, molecular oxygen (O_2) can be broken into two oxygen atoms by ultraviolet radiation from the sun. If one of these oxygen atoms has enough energy and strikes an ozone (O_3) molecule in the stratosphere, the ozone molecule is destroyed, and two oxygen molecules are created:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

This reaction is part of the natural cycle of ozone destruction and creation in the stratosphere. What is the rate of ozone destruction *for this reaction alone* at an altitude of 25 km, if the rate law for the reaction is

$$\text{rate} = 4.15 \times 10^5\ \text{L mol}^{-1}\ \text{s}^{-1}\ [O_3][O]$$

and the reactant concentrations at 25 km are the following: $[O_3] = 1.2 \times 10^{-8}\ M$ and $[O] = 1.7 \times 10^{-14}\ M$?

Analysis: We are given the rate law, so the answer to this question is merely a matter of substituting the given molar concentrations into this law.

Assembling the Tools: We will use the given rate law for the reaction along with the concentrations to calculate the rate of the reaction.

Solution: To see how the units work out, let's write all of the concentration values as well as the rate constant's units in fraction form.

$$\text{Rate} = \left(\frac{4.15 \times 10^5\ \cancel{\text{L}}}{\cancel{\text{mol}}\ \text{s}}\right) \times \left(\frac{1.2 \times 10^{-8}\ \cancel{\text{mol}}}{\cancel{\text{L}}}\right) \times \left(\frac{1.7 \times 10^{-14}\ \text{mol}}{\text{L}}\right)$$

Performing the arithmetic and canceling the units yields

$$\text{rate} = \frac{8.5 \times 10^{-17}\ \text{mol}}{\text{L s}} = 8.5 \times 10^{-17}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Is the Answer Reasonable? There's no simple check. Multiplying the powers of ten for the rate constant and the concentrations together reassures us that the rate is of the correct order of magnitude, and we can see that at least the answer has the correct units for a reaction rate.

Practice Exercises

14.5 | The rate law for the reaction $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ is

$$\text{rate} = k[NO]^2[H_2]$$

If the rate of reaction is 7.86×10^{-3} mol $L^{-1}s^{-1}$ when the concentrations of NO and H_2 are both 2×10^{-6} mol L^{-1}, (a) what is the value of the rate constant and (b) what are the units for the rate constant? (*Hint:* Note the units of the reaction rate.)

14.6 | The rate law for the decomposition of HI to I_2 and H_2 is

$$\text{rate} = k\,[HI]^2$$

At 508 °C, the rate of the reaction of HI was found to be 2.5×10^{-4} mol L^{-1} s^{-1} when the HI concentration was 0.0558 M (see Figure 14.5). (a) What is the value of k? (b) What are the units of k?

Orders of Reaction

Although a rate law's exponents are generally unrelated to the chemical equation's coefficients, they sometimes are the same by coincidence, as is the case in the decomposition of hydrogen iodide:

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

The rate law, as we've said, is

$$\text{rate} = k\,[HI]^2$$

The exponent of [HI] in the rate law—namely, 2—happens to match the coefficient of HI in the overall chemical equation, but *there is no way we could have predicted this match* *without experimental data.* Therefore, *never* simply assume the exponents and the coefficients are the same; it's a trap that many students fall into.

An exponent in a rate law is called the **order of the reaction**[1] with respect to the corresponding reactant. For instance, the decomposition of gaseous N_2O_5 into NO_2 and O_2,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

has the rate law

$$\text{rate} = k\,[N_2O_5]$$

■ Mathematicians designate equations by the exponent of the unknown, and call it the order of the equation.

■ When the exponent on a concentration term is equal to 1, it is usually omitted.

The exponent of $[N_2O_5]$ is 1, so the reaction rate is said to be *first order* with respect to N_2O_5. The rate law for the decomposition of HI has an exponent of 2 for the HI concentration, so its reaction rate is *second order* in HI. The rate law

$$\text{rate} = k[H_2SeO_3]\,[I^-]^3\,[H^+]^2$$

describes a reaction rate that is first order with respect to H_2SeO_3, third order with respect to I^-, and second order with respect to H^+.

The **overall order of a reaction** is the sum of the orders with respect to each reactant in the rate law. The decomposition of N_2O_5 is a first-order reaction. The overall order for the reaction involving H_2SeO_3 is $1 + 3 + 2 = 6$.

The exponents in a rate law are usually small whole numbers, but fractional and negative exponents are occasionally found. A negative exponent means that the concentration term really belongs in the denominator, which means that as the concentration of the species increases, the rate of reaction decreases.

There are even *zero-order* reactions. They have reaction rates that are independent of the concentration of any reactant. Zero-order reactions usually involve a small amount of a catalyst that is saturated with reactants. This is rather like the situation in a crowded supermarket with only a single checkout lane open. It doesn't matter how many people join the line; the line will move at the same rate no matter how many people are standing in it. An example of a zero-order chemical reaction is the elimination of ethyl alcohol in the body, by the liver. Regardless of the blood alcohol level, the rate of alcohol removal by the body is constant, because the number of available catalyst molecules present in the liver is constant. Another zero-order reaction is the decomposition of gaseous ammonia into H_2 and N_2 on a hot platinum surface. The rate at which ammonia decomposes is the same, regardless of its concentration in the gas.

The rate law for a zero-order reaction is simply

$$\text{rate} = k$$

where the rate constant k has units of mol $L^{-1}\,s^{-1}$. The rate constant depends on the amount, quality, and available surface area of the catalyst. For example, forcing the ammonia through hot platinum powder (with a high surface area) would cause it to decompose faster than simply passing it over a hot platinum surface.

In all of the rate laws, the rate constant, k, indicates how fast a reaction proceeds. If the value for k is large, the reaction proceeds rapidly, and if k is small, the reaction is slow. The units for k must be such that the rate calculated from the rate law has units of mol $L^{-1}\,s^{-1}$. A list of units for k, as it depends on the overall order of the reaction, is given in Table 14.2.

Table 14.2 The Units for k as It Depends on the Overall Order of the Reaction

Overall Order	Units for k
0	mol $L^{-1}\,s^{-1}$
1	s^{-1}
2	L $mol^{-1}\,s^{-1}$
3	$L^2\,mol^{-2}\,s^{-1}$
4	$L^3\,mol^{-3}\,s^{-1}$

---

[1] The reason for describing the *order* of a reaction is to take advantage of a great convenience—namely, the mathematics involved in the treatment of the data is the same for all reactions having the same order. We will not go into this very deeply, but you should be familiar with this terminology; it's often used to describe the effects of concentration on reaction rates.

Practice Exercises

14.7 | The reaction,

$$BrO_3^- + 3SO_3^{2-} \longrightarrow Br^- + 3SO_4^{2-}$$

has the rate law

$$\text{rate} = k\,[BrO_3^-]\,[SO_3^{2-}]$$

What is the order of the reaction with respect to each reactant? What is the overall order of the reaction? (*Hint:* Recall that a concentration with no exponent has, in effect, an exponent of 1.)

14.8 | A certain reaction has an experimental rate law that is found to be second order in Cl_2 and first order in NO. Write the rate law for this reaction.

14.9 | For the reaction of HCO_2H with bromine, the balanced chemical equation is

$$HCO_2H(aq) + Br_2(aq) \longrightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(aq)$$

and the rate law for this reaction is

$$\text{Rate} = k[Br_2]$$

What is the order of the reaction with respect to bromine and with respect to HCO_2H? What is the overall order of the reaction?

Obtaining Rate Laws from Experimental Data

We've mentioned several times that the exponents in the rate law of an overall reaction must be determined experimentally. *This is the only way to know for sure what the exponents are.* To determine the exponents, we study how changes in concentration affect the rate of the reaction. For example, consider again the following hypothetical reaction:

$$A + B \longrightarrow \text{products}$$

Suppose, further, that the data in Table 14.3 have been obtained in a series of five experiments. The form of the rate law for the reaction will be

$$\text{rate} = k\,[A]^n\,[B]^m$$

TOOLS

Determining the order of reactions

The values of n and m can be determined by looking for patterns in the rate data given in the table. *One of the easiest ways to reveal patterns in data is to form ratios of results using different sets of conditions.* Because this technique is quite generally useful, let's look in some detail at how it is applied to the problem of finding the rate law exponents.

For experiments 1, 2, and 3 in Table 14.3, the concentration of B has been held constant at 0.10 M. Any change in the rate for these first three experiments must be due to the change

Table 14.3 Concentration Rate Data for the Hypothetical Reaction $A + B \longrightarrow$ Products

	Initial Concentrations		
Experiment	$[A]$ (mol L^{-1})	$[B]$ (mol L^{-1})	Initial Rate of Formation of Products (mol L^{-1} s^{-1})
1	0.10	0.10	0.20
2	0.20	0.10	0.40
3	0.30	0.10	0.60
4	0.30	0.20	2.40
5	0.30	0.30	5.40

in $[A]$. The rate law tells us that when the concentration of B is held constant, the rate must be proportional to $[A]^n$, so if we take the ratio of rate laws for experiments 2 and 1, we obtain

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\ [A]_2{}^n[B]_2{}^m}{k\ [A]_1{}^n[B]_1{}^m} = \frac{k}{k}\left(\frac{[A]_2}{[A]_1}\right)^n\left(\frac{[B]_2}{[B]_1}\right)^m$$

For experiments 1 and 2, the left side of this equation is

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.40\ \cancel{\text{mol L}^{-1}\ \text{s}^{-1}}}{0.20\ \cancel{\text{mol L}^{-1}\ \text{s}^{-1}}} = 2.0$$

and on the right side of the equation the identical concentrations of B and the rate constant k cancel to give

$$\left(\frac{[A]_2}{[A]_1}\right)^n = \left(\frac{0.20\ \cancel{\text{mol L}^{-1}}}{0.10\ \cancel{\text{mol L}^{-1}}}\right)^n = 2.0^n$$

Thus, doubling $[A]$ in going from experiment 1 to experiment 2 doubles the rate, and the relationship reduces to $2.0 = 2.0^n$. For each unique combination of experiments 1, 2, and 3, we have

$$2.0 = 2.0^n \qquad \text{(for experiments 2 and 1)}$$
$$3.0 = 3.0^n \qquad \text{(for experiments 3 and 1)}$$
$$1.5 = 1.5^n \qquad \text{(for experiments 3 and 2)}$$

The only value of n that makes all of these equations true is $n = 1$. Therefore, the reaction must be first order with respect to A.

A similar method will give us the exponent on $[B]$. In the final three experiments, the concentration of B changes while the concentration of A is held constant. This time it is the concentration of B that affects the rate. Taking the ratio of rate laws for experiments 4 and 3, we have

$$\frac{\text{rate}_4}{\text{rate}_3} = \frac{k\ [A]_4{}^n[B]_4{}^m}{k\ [A]_3{}^n[B]_3{}^m}$$

The concentrations of A cancel, since $[A]_4 = [A]_3$, and both k's cancel, because the rate constant is constant, so

$$\frac{\text{rate}_4}{\text{rate}_3} = \left(\frac{[B]_4}{[B]_3}\right)^m$$

For each unique combination of experiments 3, 4, and 5, we have

$$4.0 = 2.0^m \qquad \text{(for experiments 4 and 3)}$$
$$9.0 = 3.0^m \qquad \text{(for experiments 5 and 3)}$$

The only value of m that makes these equations true is $m = 2$, so the reaction must be second order with respect to B.

If the value for the exponent is not obvious, we can also determine it by taking advantage of one of the mathematical properties of logarithms. If we take the preceding equation,

■ There is more information on using logarithms in the Appendix A.

$$\frac{\text{rate}_4}{\text{rate}_3} = \left(\frac{[B]_4}{[B]_3}\right)^m$$

and take the logarithm of both sides,

$$\log\left(\frac{\text{rate}_4}{\text{rate}_3}\right) = \log\left(\frac{[B]_4}{[B]_3}\right)^m$$

then we can move the exponent, m, outside the log term so that it multiplies the log of the ratio of the concentrations by m:

$$\log\left(\frac{\text{rate}_4}{\text{rate}_3}\right) = m\left[\log\left(\frac{[B]_4}{[B]_3}\right)\right]$$

For example, using the data from experiments 5 and 4 from Table 14.3,

$$2.25 = 1.5^m$$
$$\log(2.25) = m\log(1.5)$$
$$0.352 = m(0.176)$$
$$m = \frac{0.352}{0.176} = 2$$

Having determined the exponents for the concentration terms, we now know that the rate law for the reaction must be

$$\text{rate} = k\,[A]^1\,[B]^2 = k\,[A]\,[B]^2$$

To calculate the value of k, we substitute rate and concentration data into the rate law for any one of the sets of data.

$$k = \frac{\text{rate}}{[A]\,[B]^2}$$

Using the data from the first set in Table 14.3,

$$k = \frac{0.20\text{ mol L}^{-1}\text{ s}^{-1}}{(0.10\text{ mol L}^{-1})(0.10\text{ mol L}^{-1})^2}$$
$$= \frac{0.20\text{ mol L}^{-1}\text{ s}^{-1}}{0.0010\text{ mol}^3\text{ L}^{-3}}$$

After simplifying the units by cancellation, the value of k with the correct units is

$$k = 2.0 \times 10^2\text{ L}^2\text{ mol}^{-2}\text{ s}^{-1}$$

Table 14.4 summarizes the reasoning used to determine the order with respect to each reactant from experimental data.

Table 14.4 Relationship between the Order of a Reaction and Changes in Concentration and Rate

Factor by Which the Concentration Is Changed	Factor by Which the Rate Changes	Exponent on the Concentration Term in the Rate Law
2	Rate is unchanged.	0
3		0
4		0
2	$2 = 2^1$	1
3	$3 = 3^1$	1
4	$4 = 4^1$	1
2	$4 = 2^2$	2
3	$9 = 3^2$	2
4	$16 = 4^2$	2
2	$8 = 2^3$	3
3	$27 = 3^3$	3
4	$64 = 4^3$	3

Practice Exercises

14.10 | Use the data from the other four experiments in Table 14.3 to calculate *k* for this reaction. What do you notice about the values of *k*? What are the units for *k*? (*Hint:* Don't forget the exponents in the rate law.)

14.11 | Use the rate law determined in Practice Exercise 14.10 to describe what will happen to the reaction rate under the following conditions: (a) the concentration of *B* is tripled, (b) the concentration of *A* is tripled, and (c) the concentration of *A* is tripled and the concentration of *B* is halved.

Example 14.5

Determining the Exponents of a Rate Law

Sulfuryl chloride, SO_2Cl_2, is used to manufacture the antiseptic chlorophenol. The following data were collected on the decomposition of SO_2Cl_2 at a certain temperature.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Initial Concentration of SO_2Cl_2 (mol L^{-1})	Initial Rate of Formation of SO_2 (mol L^{-1} s^{-1})
0.100	2.2×10^{-6}
0.200	4.4×10^{-6}
0.300	6.6×10^{-6}

What are the rate law and the value of the rate constant for this reaction?

Analysis: We are asked to write the rate law for the decomposition of SO_2Cl_2, and we can only do this by using the experimental data. After we determine the exponents for the rate law, we also have to determine the rate constant, *k*, for the rate law, including the units. Finally, we will use the rate law we determined and data from one of the experiments to calculate *k*.

Assembling the Tools: The first tool we will use is the general form of the expected rate law so we can see which exponents have to be determined. Then we use the tool for determining the order of reactions from the data in Table 14.4 since the concentration is changing by a factor of two for the second reaction and three for the third reaction.

Solution: We expect the rate law to have the form

$$\text{rate} = k\,[SO_2Cl_2]^x$$

Let's examine the data from the first two experiments. Notice that when we double the concentration from 0.100 *M* to 0.200 *M*, the initial rate doubles (from 2.2×10^{-6} mol L^{-1} s^{-1} to 4.4×10^{-6} mol L^{-1} s^{-1}). If we look at the first and third experiments, we see that when the concentration triples (from 0.100 *M* to 0.300 *M*), the rate also triples (from 2.2×10^{-6} mol L^{-1} s^{-1} to 6.6×10^{-6} mol L^{-1} s^{-1}). This behavior tells us that the reaction must be first order in the SO_2Cl_2 concentration. The rate law is therefore

$$\text{rate} = k\,[SO_2Cl_2]^1 = k\,[SO_2Cl_2]$$

To evaluate *k*, we can use any of the three sets of data. Choosing the first,

$$k = \frac{\text{rate}}{[SO_2Cl_2]}$$

$$= \frac{2.2 \times 10^{-6}\ \cancel{\text{mol L}^{-1}}\ \text{s}^{-1}}{0.100\ \cancel{\text{mol L}^{-1}}} = 2.2 \times 10^{-5}\ \text{s}^{-1}$$

■ We could also use Experiments 2 and 3. From the second to the third, the rate increases by the same factor, 1.5, as the concentration, so by these data, too, the reaction must be first order.

Is the Answer Reasonable? We should get the same value of *k* by picking any other pair of rates and concentrations. Using the data from both the second and third experiments we get 2.2×10^{-5} s^{-1} each time. The fact that we get the same result each time confirms that both our rate law and calculations are reasonable.

Example 14.6
Determining the Exponents of a Rate Law

The following data were measured for the reduction of nitric oxide with hydrogen:

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Initial Concentrations (mol L^{-1})		Initial Rate of Formation of H_2O (mol L^{-1} s^{-1})
$[H_2]$	$[NO]$	
0.10	0.10	1.23×10^{-3}
0.20	0.10	2.46×10^{-3}
0.10	0.27	8.97×10^{-3}

What is the rate law for the reaction?

■ **Analysis:** This time we have two reactants. To see how their concentrations affect the rate, we must vary only one concentration at a time. Therefore, we choose two experiments in which the concentration of one reactant doesn't change and examine the effect of a change in the concentration of the other reactant. Then, we repeat the procedure for the second reactant.

■ **Assembling the Tools:** We will use the same tools we used in Example 14.5—namely, the general form of the expected rate law and the tool for determining the order of reactions from the experimental data.

■ **Solution:** We expect the rate law to have the form

$$\text{rate} = k\,[H_2]^m\,[NO]^n$$

Let's look at the first two experiments. Here the concentration of NO remains the same, so the rate is being affected by the change in the H_2 concentration. When we double the H_2 concentration, the rate doubles, so the reaction is first order with respect to H_2. This means $m = 1$.

Next, we need to pick two experiments in which the H_2 concentration doesn't change. Working with the first and third, $[NO]_1 = 0.10$ mol L^{-1} and $[NO]_3 = 0.27$ mol L^{-1}. The initial rate of reaction for the first reaction is 1.23×10^{-3} mol L^{-1} s^{-1} and for the third reaction it is 8.97×10^{-3} mol L^{-1} s^{-1}.

■ The subscripts attached to the concentrations indicate from which experiment we draw the data.

These are not simple numbers to work with, so we will have to use the ratio of the two reaction rates,

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{\cancel{k}\ \cancel{[H_2]_1^1}\,[NO]_1^n}{\cancel{k}\ \cancel{[H_2]_3^1}\,[NO]_3^n}$$

We can eliminate k and $[H_2]$, since the values are equal, in which case

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{[NO]_1^n}{[NO]_3^n}$$

$$\log\left(\frac{\text{rate}_1}{\text{rate}_3}\right) = \log\left(\frac{[NO]_1}{[NO]_3}\right)^n = n\log\left(\frac{[NO]_1}{[NO]_3}\right)$$

Now we can use the experimental data to find the value for n:

$$\log\left(\frac{1.23 \times 10^{-3}}{8.97 \times 10^{-3}}\right) = n\log\left(\frac{0.10}{0.27}\right)$$

$$\log(0.137) = n\log(0.37)$$

$$-0.863 = n(-0.431)$$

$$n = 2$$

Therefore, the rate law for the reaction is

$$\text{rate} = k\,[H_2]\,[NO]^2$$

Is the Answer Reasonable? The only data that we haven't used as a pair are the data for the second and third reactions. The value of [NO] increases by 2.7 in going from the second to the third set of data, so this should multiply the rate by 2.7^2 or 7.29, if we've found the right exponents. However, the value for $[H_2]$ halves at the same time, so this should take a rate that is otherwise four times as large and cut it in half. The net effect, then, is to make the rate of the third reaction two times as large as that of the second reaction, which is the observed rate change.

Practice Exercises

14.12 | The following reaction is investigated to determine its rate law:

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Experiments yielded the following results:

Initial Concentrations (mol L^{-1})		Initial Rate of Formation of N_2 (mol L^{-1} s^{-1})
[NO]	$[H_2]$	
0.40×10^{-4}	0.30×10^{-4}	1.0×10^{-8}
0.80×10^{-4}	0.30×10^{-4}	4.0×10^{-8}
0.80×10^{-4}	0.60×10^{-4}	8.0×10^{-8}

(a) What is the rate law for the reaction? (b) What is the value of the rate constant? (c) What are the units for the rate constant? (*Hint:* Identify the two experiments where only [NO] changes and the two experiments where only the $[H_2]$ varies.)

14.13 | Ordinary sucrose (table sugar) reacts with water in an acidic solution to produce two simpler sugars, glucose and fructose, that have the same molecular formulas.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

In a series of experiments, the following data were obtained:

Initial Sucrose Concentration (mol L^{-1})	Rate of Formation of Glucose (mol L^{-1} s^{-1})
0.10	6.17×10^{-5}
0.36	2.22×10^{-4}
0.58	3.58×10^{-4}

(a) What is the order of the reaction with respect to sucrose? (b) What is the value of the rate constant, and what are its units?

14.14 | A certain reaction has the following equation: $A + B \longrightarrow C + D$.
Experiments yielded the following results:

Initial Concentrations (mol L^{-1})		Initial Rate of Formation of *C* (mol L^{-1} s^{-1})
[*A*]	[*B*]	
0.40	0.30	1.00×10^{-4}
0.60	0.30	2.25×10^{-4}
0.80	0.60	1.60×10^{-3}

(a) What is the rate law for the reaction? (b) What is the value of the rate constant? (c) What are the units for the rate constant? (d) What is the overall order of this reaction? (*Hint:* Solve for the exponent of [*A*], then use it to solve for the exponent of [*B*].)

14.4 | Integrated Rate Laws

The rate law tells us how the speed of a reaction varies with the concentrations of the reactants. Often, however, we are more interested in how the concentrations change over time. For instance, if we were preparing some compound, we might want to know how long it will take for the reactant concentrations to drop to some particular value, so we can decide when to isolate the products.

The relationship between the concentration of a reactant and time can be derived from a rate law using calculus. By summing or "integrating" the instantaneous rates of a reaction from the start of the reaction until some specified time t, we can obtain *integrated rate laws* that quantitatively give concentration as a function of time. The form of the integrated rate law depends on the order of the reaction. The mathematical expressions that relate concentration and time in complex reactions can be complicated, so we will concentrate on using integrated rate laws for a few simple first- and second-order reactions with only one reactant.

First-Order Reactions

A **first-order reaction** is a reaction that has a rate law of the type

$$\text{rate} = k\,[A]$$

Using calculus,[2] the following equation can be derived that relates the concentration of A and time:

TOOLS

Integrated first-order rate law

$$\ln \frac{[A]_0}{[A]_t} = kt \tag{14.5}$$

The symbol "ln" means natural logarithm. The expression to the left of the equals sign is the natural logarithm of the ratio of $[A]_0$ (the initial concentration of A at $t = 0$) to $[A]_t$ (the concentration of A at a time t after the start of the reaction).

We can take the antilogarithm of both sides of Equation 14.5 and rearrange it algebraically to obtain the concentration at time t directly as a function of time:[3]

$$[A]_t = [A]_0\, e^{-kt} \tag{14.6}$$

---

[2] For a first-order reaction, the integrated rate law is obtained by calculus as follows. The instantaneous rate of change of the reactant A is given as

$$\text{rate} = \frac{-d[A]}{dt} = k[A]$$

This can be rearranged to give

$$\frac{d[A]}{[A]} = -k\,dt$$

Next we integrate between $t = 0$ and $t = t$ as the concentration of A changes from $[A]_0$ to $[A]_t$.

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -k\,dt$$

$$\ln[A]_t - \ln[A]_0 = -k\,t$$

Using the properties of logarithms, this can be rearranged to give

$$\ln \frac{[A]_0}{[A]_t} = k\,t$$

[3] Because of the nature of logarithms, if $\ln x = y$, then $e^{\ln x} = e^y$. But $e^{\ln x} = x$, so $x = e^y$. A similar relationship exists for common (i.e., base 10) logarithms. If $\log x = y$, then $10^{\log x} = x = 10^y$.

The *e* in Equation 14.6 is the base of the system of natural logarithms ($e = 2.718\ldots$). Equation 14.6 shows that the concentration of *A* decreases exponentially with time. Calculations can be done using the exponential form, Equation 14.5, or the logarithmic form, Equation 14.6. When both of the concentrations are known, it is easiest to use Equation 14.5; when we wish to calculate either $[A]_0$ or $[A]_t$, it may be easier to use Equation 14.6.

■ $[A]_t$ decreases exponentially because the product *kt* increases with time, but its negative value becomes more negative with time. As the exponent of *e* becomes a larger negative number, the value of the expression becomes smaller.

Example 14.7

Concentration–Time Calculations for First-Order Reactions

Dinitrogen pentoxide is not very stable. In the gas phase or dissolved in a nonaqueous solvent, such as carbon tetrachloride, it decomposes by a first-order reaction into dinitrogen tetroxide and molecular oxygen:

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

The rate law is

$$\text{rate} = k\,[N_2O_5]$$

At 45 °C, the rate constant for the reaction in carbon tetrachloride is $6.22 \times 10^{-4}\ s^{-1}$. If the initial concentration of N_2O_5 in a carbon tetrachloride solution at 45 °C is 0.500 *M*, what will its concentration be after exactly one hour (i.e., 1.00 hr)?

■ **Analysis:** We're dealing with a first-order reaction and the relationship between concentration and time, and we are looking for a concentration after one hour. We are given an initial concentration, 0.500 *M*, and the rate constant for the reaction, $6.22 \times 10^{-4}\ s^{-1}$.

■ **Assembling the Tools:** The tool we have to apply is either Equation 14.5 or 14.6, the integrated rate law for first-order reactions. Specifically, we have to solve for an unknown concentration. The easiest form of the equation to use when one of the unknowns is a concentration term is Equation 14.6. In performing the calculation, we have to remember that the unit of *k* involves seconds, not hours, so we must convert the given time, 1.00 hr, into seconds ($1.00\ \text{hr} = 3.60 \times 10^3\ s$).

■ **Solution:** Let's begin by listing the data.

$$[N_2O_5]_0 = 0.500\ M \qquad [N_2O_5]_t = ?\ M$$
$$k = 6.22 \times 10^{-4}\ s^{-1} \qquad t = 3.60 \times 10^3\ s$$

Using Equation 14.6,[4]

$$\begin{aligned}[N_2O_5]_t &= [N_2O_5]_0\, e^{-kt}\\ &= (0.500\ M) \times e^{-(6.22 \times 10^{-4}\ s^{-1}) \times (3.60 \times 10^3)\ s}\\ &= (0.500\ M) \times e^{-2.24}\\ &= (0.500\ M) \times 0.11\\ &= 0.055\ M\end{aligned}$$

■ Calculating $e^{-2.44}$ is a simple operation using a scientific calculator. In most cases it is the inverse of the ln function.

After one hour, the concentration of N_2O_5 will have decreased to 0.0532 *M*.

The calculation could also have been done using Equation 14.5. We would begin by solving for the concentration ratio, substituting values for *k* and *t*:

$$\begin{aligned}\ln\left(\frac{[N_2O_5]_0}{[N_2O_5]_t}\right) &= (6.22 \times 10^{-4}\ s^{-1}) \times (3.60 \times 10^3\ s)\\ &= 2.24\end{aligned}$$

---

[4] There are special rules for significant figures for logarithms and antilogarithms. In writing the logarithm of a quantity, the number of digits written *after the decimal point* equals the number of significant figures in the quantity. Raising *e* to the −2.24 power is the same as taking the antilogarithm of −2.24. Because the quantity −2.24 has two digits after the decimal, the antilogarithm, 0.1064 . . ., must be rounded to 0.11 to show just two significant figures.

To take the antilogarithm (antiln), we raise *e* to the 2.24 power:

$$\text{antiln}\left[\ln\left(\frac{[N_2O_5]_0}{[N_2O_5]_t}\right)\right] = \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$\begin{aligned}\text{antiln}\,(2.24) &= e^{2.24}\\ &= 9.4 \text{ (rounding to 2 significant figures)}\end{aligned}$$

This means that

$$\frac{[N_2O_5]_0}{[N_2O_5]_t} = 9.4$$

Now, we can substitute the known concentration, $[N_2O_5]_0 = 0.500\ M$. This gives

$$\frac{0.500\ M}{[N_2O_5]_t} = 9.4$$

Solving for $[N_2O_5]_t$ gives

$$\begin{aligned}[N_2O_5]_t &= \frac{0.500\ M}{9.4}\\ &= 0.053\ M\end{aligned}$$

The answers obtained by the two methods differ slightly because of "rounding errors." You can see that using Equation 14.6, the exponential form, is much easier for working this particular problem.

■ **Is the Answer Reasonable?** Notice that the final concentration of N_2O_5, the reactant in the reaction, is *less* than its initial concentration. You'd know that you made a huge mistake if the calculated final concentration was greater than the initial 0.500 *M* because reactants are consumed in chemical reactions. Also, we obtained essentially the same answer using both Equations 14.5 and 14.6, so we can be confident it's correct. (If you're faced with a problem like this, you don't have to do it both ways; we just wanted to show that either equation could be used.)

Practice Exercises

14.15 | When designing a consumer product, it is desirable that it have a two-year shelf life. Often this means that the active ingredient in the product should not decrease by more than 5% in two years. If the reaction is first order, what rate constant must the decomposition reaction of the active ingredient have? (*Hint:* What are the initial and final percentages of active ingredient?)

14.16 | In Practice Exercise 14.13, the reaction of sucrose with water in an acidic solution was described.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The reaction is first order with a rate constant of $6.17 \times 10^{-4}\ s^{-1}$ at 35 °C, when $[H^+] = 0.10\ M$. Suppose that in an experiment the initial sucrose concentration was 0.40 *M*. (a) What will the concentration be after exactly 2 hours (i.e., 2.00 h)? (b) How many minutes will it take for the concentration of sucrose to drop to 0.30 *M*?

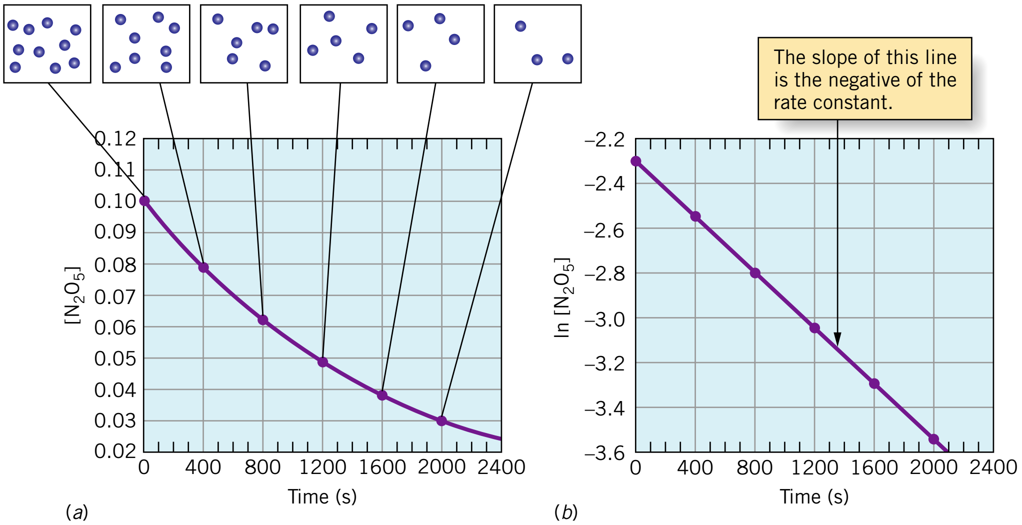
Determining Rate Constants of First-Order Reactions

Using the properties of logarithms,[5] Equation 14.5 can be rewritten as the following difference in logarithms:

$$\ln[A]_0 - \ln[A]_t = kt$$

---

[5] The logarithm of a quotient, $\ln\frac{a}{b}$, can be written as the difference, $\ln a - \ln b$.



The slope of this line is the negative of the rate constant.

Figure 14.6 | **The decomposition of N_2O_5.** (*a*) A graph of concentration versus time for the decomposition at 45 °C. (*b*) A straight line is obtained if the logarithm of the concentration is plotted versus time. The slope of this line equals the negative of the rate constant for the reaction.

This difference can then be rearranged into a form that corresponds to the equation for a straight line.

$$\begin{array}{ccccc} \ln[A]_t & = & -kt & + & \ln[A]_0 \\ \updownarrow & & \updownarrow\updownarrow & & \updownarrow \\ y & = & mx & + & b \end{array}$$

■ The equation for a straight line is usually written

$$y = mx + b$$

where *x* and *y* are variables, *m* is the slope, and *b* is the intercept of the line with the *y* axis.

A plot of the values of $\ln[A]_t$ (vertical axis) versus values of t (horizontal axis) should give a straight line that has a slope equal to $-k$, the negative of the rate constant. Such a plot is illustrated in Figure 14.6 for the decomposition of N_2O_5 into N_2O_4 and O_2 in carbon tetrachloride solvent.

One method of determining whether a reaction is first order with respect to a reactant is to plot the natural logarithm of the concentration as it changes over time and see whether a straight line is obtained.

Half-Life of a Reaction

The *half-life* of a reactant is a convenient way to describe how fast it reacts, particularly for a first-order process. A reactant's **half-life, $t_{1/2}$**, is the amount of time required for half of the reactant to disappear. A rapid reaction has a short half-life because half of the reactant disappears quickly. The equations for half-lives depend on the order of the reaction.

When we state the order of a reaction, we are referring to the overall reaction. Otherwise we state "with respect to" a specific reactant. When a reaction is first order, the half-life of the reactant can be obtained by setting $[A]_t$ equal to one-half of $[A]_0$ and using Equation 14.5.

$$[A]_t = \tfrac{1}{2}[A]_0$$

Substituting $\frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.5, we have

$$\ln\frac{[A]_0}{\frac{1}{2}[A]_0} = kt_{1/2}$$

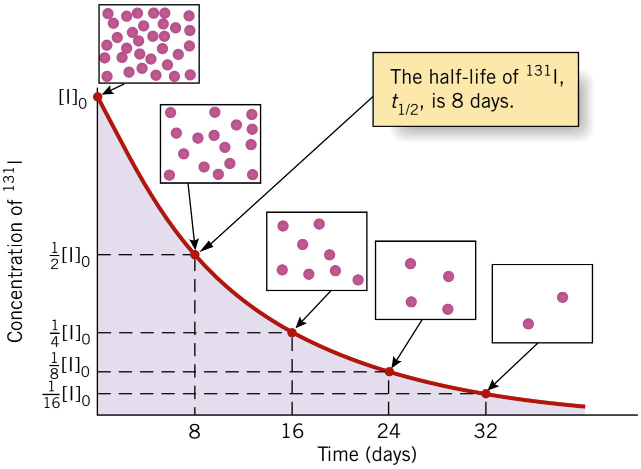
Note that the left-hand side of the equation simplifies to ln 2, so solving the equation for $t_{1/2}$ yields Equation 14.7:

$$t_{1/2} = \frac{\ln 2}{k} \qquad \textbf{(14.7)}$$

■ Because ln 2 equals 0.693, Equation 14.7 is sometimes written $t_{1/2} = \dfrac{0.693}{k}$

TOOLS

Half-lives of first-order reactions



The half-life of ^{131}I, $t_{1/2}$, is 8 days.

Figure 14.7 | **First-order radioactive decay of iodine-131.** The initial concentration of the isotope is represented by $[I]_0$.

Because k is a constant for a given reaction, the half-life is also a constant for any particular first-order reaction (at any given temperature). Remarkably, in other words, *the half-life of a first-order reaction is not affected by the initial concentration of the reactant.* This can be illustrated by one of the most common first-order events in nature, the change that radioactive isotopes undergo during radioactive "decay." In fact, you may have heard the term *half-life* used in reference to the life spans of radioactive substances.

Iodine-131 is an unstable, radioactive isotope of iodine and undergoes a nuclear reaction, emitting radiation[6] (more information about nuclear chemistry is presented in Chapter 21, Nuclear Chemistry). The intensity of the radiation emitted decreases, or *decays,* with time, as shown in Figure 14.7. Notice that the time it takes for the first half of the ^{131}I to disappear is eight days. During the next eight days, half of the remaining ^{131}I disappears, and so on. Regardless of the initial amount, it takes eight days for half of that amount of ^{131}I to disappear, which means that the half-life of ^{131}I is a constant, and the reaction is first-order.

Example 14.8
Half-Life Calculations

Suppose a patient is given a certain amount of iodine-131 as part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive iodine-131 is 8.02 days, what fraction of the initial iodine-131 would be present in a patient after 25 days if none of it were eliminated through natural body processes?

■ **Analysis:** We've learned that radioactive iodine-131 decays by a first-order process with a constant half-life. We can use the half-life to calculate the rate constant, k, for the reaction and then use the rate constant to calculate the amount of material left.

■ **Assembling the Tools:** We will need to use Equation 14.7 to determine the rate constant from the half-life,

$$t_{1/2} = \frac{\ln 2}{k}$$

and then Equation 14.5 to find the amount of material remaining after 25 days:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

---

[6] Iodine-131 is used in the diagnosis of thyroid disorders. The thyroid gland is a small organ located just below the "Adam's apple" and astride the windpipe. It uses iodide ion to make a hormone, so when a patient is given a dose of $^{131}I^-$ mixed with nonradioactive I^-, both ions are taken up by the thyroid gland. The change in (temporary) radioactivity of the gland is a measure of thyroid activity.

Solution: We will start by finding the first-order rate constant, k, which we can obtain from the half-life by rearranging Equation 14.7 (note that we keep one extra significant figure until the end):

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{8.02 \text{ days}} = 0.0864 \text{ day}^{-1}$$

Then, we can use Equation 14.5 to compute the fraction, $\frac{[A]_0}{[A]_t}$,

$$\ln\frac{[A]_0}{[A]_t} = kt = (0.0864 \text{ day}^{-1})(25 \text{ days}) = 2.160$$

This is a logarithm, so it should have three decimal places for the three significant figures.

Taking the antilogarithm of both sides, we have

$$\frac{[A]_0}{[A]_t} = e^{2.160} = 8.67 = 8.7$$

The initial concentration, $[A]_0$, is 8.7 times as large as the concentration after 25.0 days, so the fraction remaining after 25 days is

$$\frac{1}{8.7} \text{ or } 0.11$$

Is the Answer Reasonable? A period of 24 days is exactly three 8.0 day half-lives, and 25 is very close to 24. Therefore, we can use the value of 24 days and apply the half-life concept three times. If we take the fraction initially present to be 1, we can set up the following table:

Half-life	0	1	2	3
Fraction	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$

The fraction remaining after n half-lives is $\left(\frac{1}{2}\right)^n$, or simply $\frac{1}{2^n}$.

Half of the iodine-131 is lost in the first half-life, half of that disappears in the second half-life, and so on. Therefore, the fraction remaining after three half-lives is $\frac{1}{8}$ which is very close to our value of $\frac{1}{8.7}$.

Practice Exercises

14.17 | In Practice Exercise 14.13, the reaction of sucrose with water was found to be first order with respect to sucrose. The rate constant under the conditions of the experiments was 6.17×10^{-4} s^{-1}. Calculate the value of $t_{1/2}$ for this reaction in minutes. How many minutes would it take for three-quarters of the sucrose to react? (*Hint*: What fraction of the sucrose remains?)

14.18 | From the answer to Practice Exercise 14.15, determine the half-life of an active ingredient that has a shelf life of 2.00 years.

14.19 | The radioactive isotope, phosphorus-32, has a half-life of 14.26 days. How much phosphorus-32 will remain after 60 days?

Carbon-14 Dating

Carbon-14 is a radioactive isotope with a half-life of 5730 years and a rate constant, k, of 1.21×10^{-4} yr^{-1}. It is formed in small amounts in the upper atmosphere by the action of cosmic rays on nitrogen atoms. Once formed, the carbon-14 diffuses into the lower atmosphere. It becomes oxidized to carbon dioxide and enters earth's biosphere by means of photosynthesis. Carbon-14 thus becomes incorporated into plant substances and into the materials of animals that eat plants. As the carbon-14 decays, more is ingested by the living thing. The net effect is an overall steady-state availability of carbon-14 in the global system. As long as the plant or animal is alive, its ratio of carbon-14 atoms to carbon-12 atoms is constant. At death, an organism's remains have as much carbon-14 as they can ever have, and they now slowly lose this carbon-14 by radioactive decay. The decay is a first-order process with a rate independent of the *number* of original carbon atoms. The ratio of carbon-14 to carbon-12, therefore, can be related to the years that have elapsed between the time of death and the time of the measurement. The critical assumption in carbon-14 dating is that the steady-state availability of carbon-14 from the atmosphere has remained largely unchanged since the specimen stopped living.[7]

- In all dating experiments, the amounts of sample are extremely small, and extraordinary precautions must be taken to avoid contaminating specimens with "modern" materials.
- Willard F. Libby won the Nobel Prize in chemistry in 1960 for his discovery of the carbon-14 method for dating ancient objects.

In contemporary biological samples, the ratio $^{14}C/^{12}C$ is about 1.2×10^{-12}. Thus, each fresh 1.0 g sample of biological carbon in equilibrium with the $^{14}CO_2$ of the atmosphere has a ratio of 5.8×10^{10} atoms of carbon-14 to 4.8×10^{22} atoms of carbon-12. The ratio decreases by a factor of 2 for each half-life period of ^{14}C.

The dating of an object makes use of the fact that radioactive decay is a first-order process. If we let r_0 stand for the $^{14}C/^{12}C$ ratio at the time of death of the carbon-containing species and r_t stand for the $^{14}C/^{12}C$ ratio now, after the elapse of t years, we can substitute into Equation 14.5 to obtain

$$\ln \frac{r_0}{r_t} = kt \qquad \textbf{(14.8)}$$

where k is the rate constant for the decay (the *decay constant* for ^{14}C) and t is the elapsed time. We can now substitute $1.21 \times 10^{-4}\ \text{yr}^{-1}$ for k into Equation 14.8 to give

TOOLS

Carbon-14 dating

$$\ln \frac{r_0}{r_t} = (1.21 \times 10^{-4}\ \text{yr}^{-1})t \qquad \textbf{(14.9)}$$

Equation 14.9 can be used to calculate the age of a once-living object if its current $^{14}C/^{12}C$ ratio can be measured.

We have to realize here that we are not using the number of disintegrating nuclei, but the ratio of $^{14}C/^{12}C$, which is an intensive property. We need to use intensive properties to calculate the age of the object, since the size of the sample cannot be a determining factor.

Example 14.9

Calculating the Age of an Object by ^{14}C Dating

Using a mass spectrometer, a sample of an ancient wooden object was found to have a ratio of ^{14}C to ^{12}C equal to 3.3×10^{-13} as compared to a contemporary biological sample, which has a ratio of ^{14}C to ^{12}C of 1.2×10^{-12}. What is the age of the object?

Analysis: We are given the ratio of ^{14}C to ^{12}C and asked to find the age of the object.

Assembling the Tools: The tool we will use is Equation 14.9, and substitute the values given with $r_0 = 1.2 \times 10^{-12}$ and $r_t = 3.3 \times 10^{-13}$.

Solution: The contemporary ratio of ^{14}C to ^{12}C was given as 1.2×10^{-12}. This corresponds to r_0 in Equation 14.9. Substituting into Equation 14.9 gives

$$\ln \frac{1.2 \times 10^{-12}}{3.3 \times 10^{-13}} = (1.21 \times 10^{-4}\ \text{yr}^{-1})t$$

$$\ln(3.6) = (1.21 \times 10^{-4}\ \text{yr}^{-1})t$$

Solving for t gives an age of 1.1×10^4 years (11,000 years).

Is the Answer Reasonable? We've been told that the object is ancient, so 11,000 years old seems to make sense. (Also, if you had substituted incorrectly into Equation 14.9, the answer would have been negative, and that certainly doesn't make sense!)

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[7] The available atmospheric pool of carbon-14 atoms fluctuates somewhat with the intensities of cosmic ray showers, with slow, long-term changes in earth's magnetic field, and with the huge injections of carbon-12 into the atmosphere from the large-scale burning of coal and petroleum in the 1900s. To reduce the uncertainties in carbon-14 dating, results of the method have been correlated with dates made by tree-ring counting. For example, an uncorrected carbon-14 dating of a Viking site at L'Anse aux Meadows, Newfoundland, gave a date of AD 895 ± 30. When corrected, the date of the settlement became AD 997, almost exactly the time indicated in Icelandic sagas for Leif Eriksson's landing at "Vinland," now believed to be the L'Anse aux Meadows site.

Practice Exercises

14.20 | The ^{14}C content of an ancient piece of wood was found to be one-tenth of that in living trees. How many years old is this piece of wood ($t_{1/2} = 5730$ for ^{14}C)? (*Hint:* Recall the relationship between the integrated rate equation and half-life.)

14.21 | The calibration curves for carbon-14 dating are constantly being updated. Before 2010, when using carbon-14 dating, samples that had decayed less than 5% and those that had decayed more than 95% may have had unacceptably large uncertainties. How many years before the present could carbon-14 be used for dating an object using the 5% and 95% limits?

Second-Order Reactions

For simplicity, we will only consider a **second-order reaction** with a rate law with only one reactant,

$$\text{rate} = k\,[B]^2$$

The relationship between concentration and time for a reaction with such a rate law is given by Equation 14.10, an equation that is quite different from that for a first-order reaction.

$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt \qquad (14.10)$$

TOOLS

Integrated second-order rate law

$[B]_0$ is the initial concentration of B and $[B]_t$ is the concentration at time t.

Example 14.10

Concentration–Time Calculations for Second-Order Reactions

Nitrosyl chloride, NOCl, decomposes slowly to NO and Cl_2:

$$2\text{NOCl} \longrightarrow 2\text{NO} + \text{Cl}_2$$

The rate law for this reaction is second order in NOCl:

$$\text{rate} = k\,[\text{NOCl}]^2$$

The rate constant k equals 0.020 L mol^{-1} s^{-1} at a certain temperature. If the initial concentration of NOCl in a closed reaction vessel is 0.050 M, what will the concentration be after 35 minutes?

■ **Analysis:** We're given a rate law that is for a second-order reaction. We must calculate $[\text{NOCl}]_t$, the molar concentration of NOCl, after 35 minutes (i.e., 2100 s).

■ **Assembling the Tools:** Our tool for doing this is Equation 14.10, the integrated rate law for second-order reactions.

■ **Solution:** Let's begin by tabulating the data:

$$[\text{NOCl}]_0 = 0.050\ M \qquad [\text{NOCl}]_t = ?\ M$$
$$k = 0.020\ \text{L mol}^{-1}\ \text{s}^{-1} \qquad t = 2100\ \text{s}$$

The equation we wish to substitute into is

$$\frac{1}{[\text{NOCl}]_t} - \frac{1}{[\text{NOCl}]_0} = kt$$

Making the substitutions gives

$$\frac{1}{[\text{NOCl}]_t} - \frac{1}{0.050\ \text{mol L}^{-1}} = (0.020\ \text{L mol}^{-1}\ \text{s}^{-1}) \times (2100\ \text{s})$$

Solving for $1/[\text{NOCl}]_t$ gives

$$\frac{1}{[\text{NOCl}]_t} - 20 \text{ L mol}^{-1} = 42 \text{ L mol}^{-1}$$

$$\frac{1}{[\text{NOCl}]_t} = 62 \text{ L mol}^{-1}$$

Taking the reciprocals of both sides gives us the value of $[\text{NOCl}]_t$:

$$[\text{NOCl}]_t = \frac{1}{62 \text{ L mol}^{-1}} = 0.016 \text{ mol L}^{-1} = 0.016\ M$$

The molar concentration of NOCl has decreased from 0.050 *M* to 0.016 *M* after 35 minutes.

■ **Is the Answer Reasonable?** The concentration of NOCl has decreased, so the answer appears to be reasonable.

Practice Exercises

14.22 | For the reaction in Example 14.10, determine how many minutes it would take for the NOCl concentration to drop from 0.040 *M* to 0.010 *M*. (*Hint:* In solving Equation 14.10, time must be a positive value.)

14.23 | A sample of nitrosyl chloride was collected for analysis at 10:35 AM. At 3:15 PM the same day, the sample was analyzed and was found to contain 0.0035 *M* NOCl. What was the concentration of NOCl at the time the sample was collected?

Second-Order Rate Constants

The rate constant *k* for a second-order reaction, one with a rate following Equation 14.10, can be determined graphically by a method similar to that used for a first-order reaction. We can rearrange Equation 14.10 so that it corresponds to an equation for a straight line:

$$\begin{array}{ccccc} \dfrac{1}{[B]_t} & = & kt & + & \dfrac{1}{[B]_0} \\ \updownarrow & & \updownarrow\updownarrow & & \updownarrow \\ y & = & mx & + & b \end{array}$$

When a reaction is second order, a plot of $1/[B]_t$ versus *t* should yield a straight line having a slope *k*. This is illustrated in Figure 14.8 for the decomposition of HI, using data in Table 14.1.

Half-Lives of Second-Order Reactions

The half-life of a second-order reaction *does* depend on initial reactant concentrations. We can see this by examining Figure 14.8, which follows the decomposition of gaseous HI, a second-order reaction. The reaction begins with a hydrogen iodide concentration of 0.10 *M*. After 125 seconds, the concentration of HI drops to 0.050 *M*, so 125 s is the observed half-life when the initial concentration of HI is 0.10 *M*. If we then take 0.050 *M* as the next "initial" concentration, we find that it takes 250 seconds (at a *total* elapsed time of 375 seconds) to drop to 0.025 *M*. If we cut the initial concentration in half, from 0.10 *M* to 0.050 *M*, the half-life doubles, from 125 to 250 seconds.

It can be shown that for a second-order reaction of the type we're studying, the half-life is inversely proportional to the initial concentration of the reactant. The half-life is related to the rate constant by Equation 14.11.

$$t_{1/2} = \frac{1}{k \times (\text{initial concentration of reactant})} \tag{14.11}$$

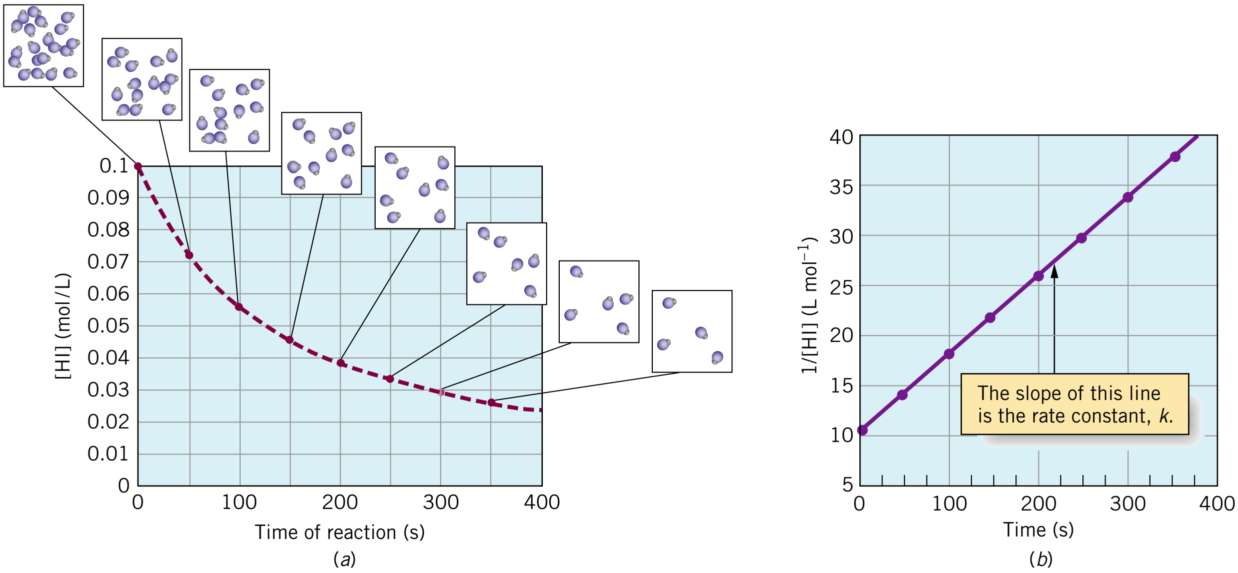


Figure 14.8 | **Second-order kinetics.** (*a*) A graph of concentration versus time for the decomposition of HI for the data in Table 14.1. (*b*) A straight line is obtained if 1/[HI] is plotted versus time.

Zero-Order Reactions

Zero-order reactions have an exponent of zero on the concentration term, so they do not depend on the concentration of the reactant:

$$\text{rate} = k\,[A]^0 = k$$

When the concentration of the reactant is plotted versus time, it will give a straight line if the reaction is a zero-order reaction, since the integrated rate law equation is

$$[A]_t = -kt + [A]_0 \tag{14.12}$$

TOOLS Integrated zero-order rate law

This can also be plotted in a similar fashion to the first-order and second-order reactions, which will give the rate constant, *k*, as the negative of the slope. The half-life expression for a zero-order reaction can be determined by substituting $[A]_t = \frac{1}{2}[A]_0$ into Equation 14.12 and solving the equation to get

$$t_{1/2} = \frac{1}{k}\,\frac{[A]_0}{2}$$

Graphical Interpretation of Orders of Reactions

For zero-order reactions to yield a straight line, the concentration of the reactant is plotted versus time and the negative of the slope is the rate constant. First-order reactions have a linear graph when the natural log of the concentration of the reactant is plotted versus time and the negative slope of the line is the rate constant. Second-order reactions require the inverse of the concentration to be plotted versus time to give a straight line, and the slope of the line is the rate constant. All of this information is summarized in Table 14.5.

Table 14.5 Graphical Interpretation of Orders of Reactions

Order of Reaction	Straight-Line Plot	Rate Constant, k	Half-Life Dependence
0	$[X]$ versus time	Negative slope of line	Depends on initial concentration
1	$\ln[X]$ versus time	Negative slope of line	No dependence on concentration
2	$1/[X]$ versus time	Slope of line	Depends on initial concentration

Example 14.11
Half-Life Calculations

The reaction $2HI(g) \longrightarrow H_2(g) + I_2(g)$ has the rate law, rate $= k\,[HI]^2$, with $k = 0.079$ L mol^{-1} s^{-1} at 508 °C. What is the half-life for this reaction at this temperature when the initial HI concentration is 0.10 *M*?

Analysis: The rate law tells us that the reaction is second-order, and we are asked for the half-life for this reaction. Keep in mind that for second-order reactions, the half-life depends on the initial concentration.

Assembling the Tools: To calculate the half-life, we need to use Equation 14.11 as the tool to solve this problem.

Solution: The initial concentration is 0.10 mol L^{-1}; $k = 0.079$ L mol^{-1} s^{-1}. Substituting these values into Equation 14.11 gives

$$\begin{aligned} t_{1/2} &= \frac{1}{(0.079\ \cancel{\text{L}}\ \cancel{\text{mol}^{-1}}\ \text{s}^{-1})(0.10\ \cancel{\text{mol}}\ \cancel{\text{L}^{-1}})} \\ &= 1.3 \times 10^2\ \text{s} \end{aligned}$$

Is the Answer Reasonable? To estimate the answer, we round the 0.079 to 0.1, so the estimated answer is $\dfrac{1}{0.1 \times 0.1} = 100$. This is close to our calculated value. In addition, we check that the units cancel to leave only the seconds units. Both of these checks support our answer.

Practice Exercises

14.24 | The reaction $2NO_2 \longrightarrow 2NO + O_2$ is second order with respect to NO_2. If the initial concentration of $NO_2(g)$ is 6.54×10^{-4} mol L^{-1}, what is the rate constant if the initial reaction rate is 4.42×10^{-7} mol L^{-1} s^{-1}? What is the half-life of this system? (*Hint:* Start by setting up and solving the rate law before the integrated equation.)

14.25 | Suppose that the value of $t_{1/2}$ for a certain reaction was found to be independent of the initial concentration of the reactants. What could you say about the order of the reaction? Justify your answer.

14.5 | Molecular Basis of Collision Theory

As a rule, the rate of a chemical reaction increases by a factor of about 2 or 3 for each 10 °C increase in temperature, although the actual amount of increase differs from one reaction to another. Temperature evidently has a strong effect on reaction rate. To understand why, we need to develop theoretical models that explain our observations. One of the simplest models is called *collision theory*.

Collision Theory

The basic postulate of **collision theory** is that the rate of a reaction is proportional to the number of *effective* collisions per second among the reactant molecules. An **effective collision** is one that actually gives product molecules. Anything that can increase the frequency of effective collisions should, therefore, increase the rate.

One of the several factors that influences the number of effective collisions per second is *concentration*. As reactant concentrations increase, the number of collisions per second of all types, including effective collisions, cannot help but increase. We'll return to the significance of concentration in Section 14.8.

Not *every* collision between reactant molecules actually results in a chemical change. We know this because the reactant atoms or molecules in a gas or a liquid undergo an enormous number of collisions per second with each other. If every collision were effective, all reactions would be over in an instant. *Only a very small fraction of all of the collisions can really lead to a net change*. Why is this so?

Molecular Orientation

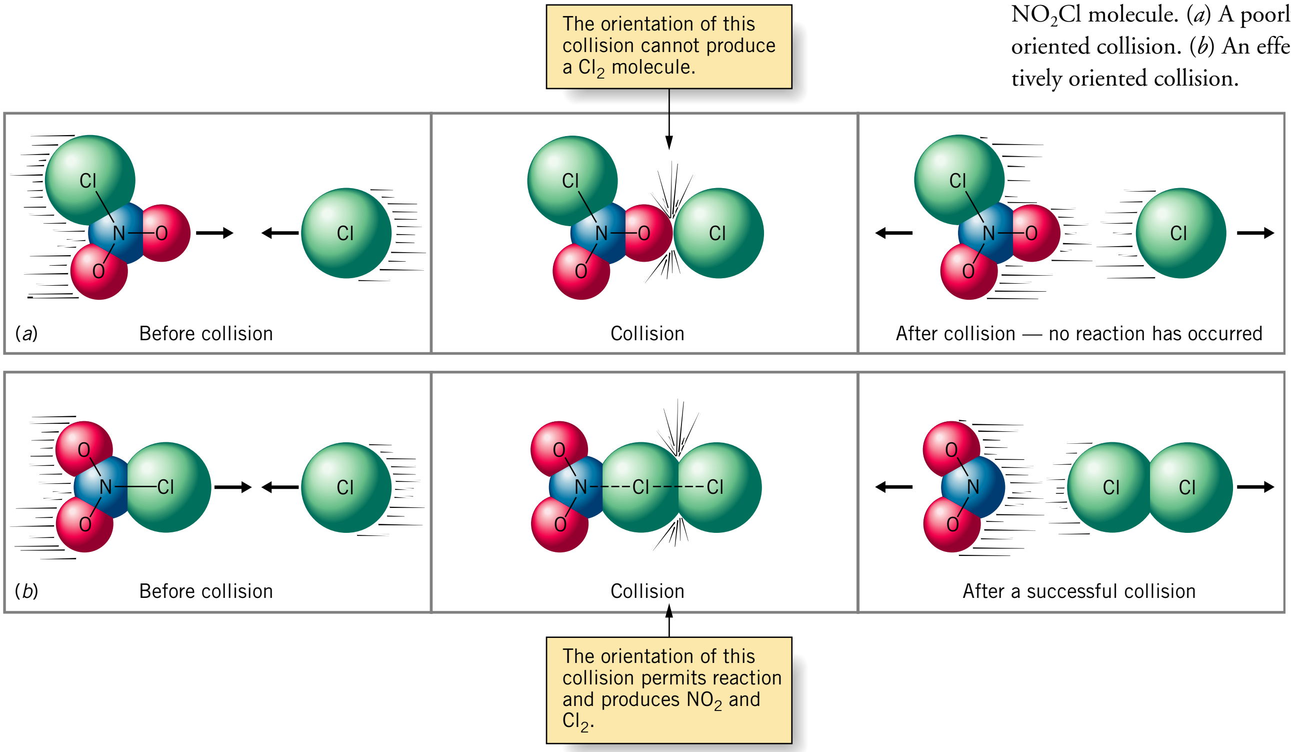
In most reactions, when two reactant molecules collide, they must be oriented correctly for a reaction to occur. For example, the reaction represented by the following balanced chemical equation,

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

appears to proceed by a two-step sequence of reactions. One step involves the collision of an NO_2Cl molecule with a chlorine atom:

$$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$$

The orientation of the NO_2Cl molecule, when hit by the Cl atom, is important (see Figure 14.9). The poor orientation shown in Figure 14.9*a* cannot result in the formation



The orientation of this collision cannot produce a Cl_2 molecule.

(*a*) Before collision

Collision

After collision — no reaction has occurred

(*b*) Before collision

Collision

After a successful collision

The orientation of this collision permits reaction and produces NO_2 and Cl_2.

Figure 14.9 | **The importance of molecular orientation during a collision in a reaction.** The key step in the decomposition of NO_2Cl to NO_2 and Cl_2 is the collision of a Cl atom with a NO_2Cl molecule. (*a*) A poorly oriented collision. (*b*) An effectively oriented collision.

of Cl_2 because the two Cl atoms are not being brought close enough together for a new Cl—Cl bond to form as an N—Cl bond breaks. Figure 14.9*b* shows the necessary orientation if the collision of NO_2Cl and Cl is to effectively lead to products.

Molecular Kinetic Energy

Not all collisions, even those correctly oriented, are energetic enough to result in products, and this is the major reason that only a small percentage of all collisions actually lead to chemical change. The colliding particles must carry into the collision a certain minimum combined molecular kinetic energy, called the **activation energy, E_a**. In a successful collision, activation energy changes over to potential energy as the particles hit each other and chemical bonds in the reactants reorganize into those of the products. For most chemical reactions, the activation energy is quite large, and only a small fraction of all well-oriented, colliding molecules have it.

■ At the start of the reaction described by Figure 14.5, only about one of every billion billion (10^{18}) collisions leads to a net chemical reaction. In each of the other collisions, the reactant molecules just bounce off each other.

We can understand the existence of activation energy by studying in detail what actually takes place during a collision. For old bonds to break and new bonds to form, the atomic nuclei within the colliding particles must get close enough together. The molecules on a collision course must, therefore, be moving with a combined kinetic energy great enough to overcome the natural repulsions between electron clouds. Otherwise, the molecules simply veer away or bounce apart. Only fast molecules with large kinetic energies can collide with enough collision energy to enable their nuclei and electrons to overcome repulsions and thereby reach the positions required for the bond breaking and bond making that the chemical change demands, as shown in Figure 14.10.

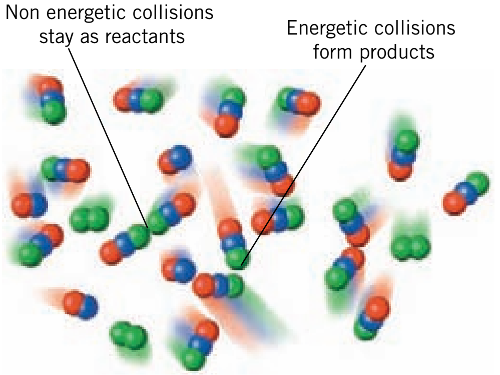

Non energetic collisions stay as reactants
Energetic collisions form products

Figure 14.10 | **The energetics of collisions that lead to products.**

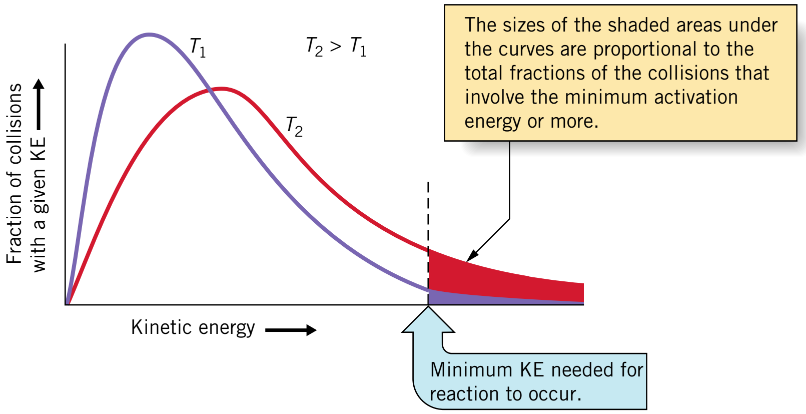
Effect of Temperature

With the concept of activation energy, we can now explain why the rate of a reaction increases with increasing temperature. We'll use the two kinetic energy curves in Figure 14.11, each corresponding to a different temperature for the same mixture of reactants. Just like the graphs in Figure 12.18, each curve is a plot of the different *fractions* of all collisions (vertical axis) that have particular values of kinetic energy (horizontal axis). Notice what happens to the plots when the temperature is increased; the maximum point shifts to the right and the curve flattens somewhat. However, *a modest increase in temperature generally does not affect the reaction's activation energy*. In other words, as the curve flattens and shifts to the right with an increase in temperature, the value of E_a stays the same.

■ The fraction of molecules, f_{KE}, having or exceeding the activation energy, E_a, is given by the expression

$$\ln f_{KE} = \frac{-E_a}{RT}$$

The shaded areas under the curves in Figure 14.11 represent the sum of all those fractions of the total collisions that equal or exceed the activation energy. This sum—we could call it the *reacting fraction*—is greater at the higher temperature than at the lower temperature because a significant fraction of the curve shifts beyond the activation energy in even a modest change to a higher temperature. In other words, at the higher temperature, more of the collisions occurring each second results in a chemical change, so the reaction is faster at the higher temperature.



The sizes of the shaded areas under the curves are proportional to the total fractions of the collisions that involve the minimum activation energy or more.

Minimum KE needed for reaction to occur.

Figure 14.11 | **Kinetic energy distributions for a reaction mixture at two different temperatures.**

On the molecular scale, we can write an equation that summarizes the three factors involved in the collision theory as

$$\text{reaction rate(molecules L}^{-1}\text{ s}^{-1}) = N \times f_{\text{orientation}} \times f_{\text{KE}}$$

where N represents the collisions per second per liter of the mixture, which is approximately 10^{27} s^{-1}. The two other terms represent the fraction of collisions with the correct orientation, $f_{\text{orientation}}$, and the fraction of collisions with the required total kinetic energy, f_{KE}. To convert this to the laboratory scale where the rate of the reaction has units of mol L^{-1} s^{-1}, we divide the equation by Avogadro's number:

$$\text{reaction rate (mol L}^{-1}\text{ s}^{-1}) = \frac{\text{reaction rate(}\cancel{\text{molecules}}\text{ L}^{-1}\text{ s}^{-1})}{6.02 \times 10^{23}\ (\cancel{\text{molecules}}\text{ mol}^{-1})}$$

14.6 | Molecular Basis of Transition State Theory

Transition state theory is used to explain in detail what happens when reactant molecules come together in a collision. Most often, those in a head-on collision slow down, stop, and then fly apart unchanged. When a collision does cause a reaction, the particles that separate are those of the products. Regardless of what happens to them, however, as the molecules on a collision course slow down, their total kinetic energy decreases as it changes into potential energy (PE). It's like the momentary disappearance of the kinetic energy of a tennis ball when it hits the racket. In the deformed racket and ball, this energy becomes potential energy, which soon changes back to kinetic energy as the ball takes off in a new direction.

Potential Energy Diagrams

To visualize the relationship between activation energy and the development of total potential energy, we sometimes use a *potential energy diagram* (Figure 14.12). The vertical axis represents changes in *potential* energy as the *kinetic* energy of the colliding particles changes over to this form. The horizontal axis is called the **reaction coordinate**, and it represents the extent to which the reactants have changed to the products. It helps us follow the path taken by the reaction as reactant molecules come together and change into product molecules. Activation energy appears as a potential energy "hill" or barrier between the reactants and products. Only colliding molecules, properly oriented, which can deliver sufficient kinetic energy that can be converted into potential energy at least as large as E_a, are able to climb over the hill and produce products.

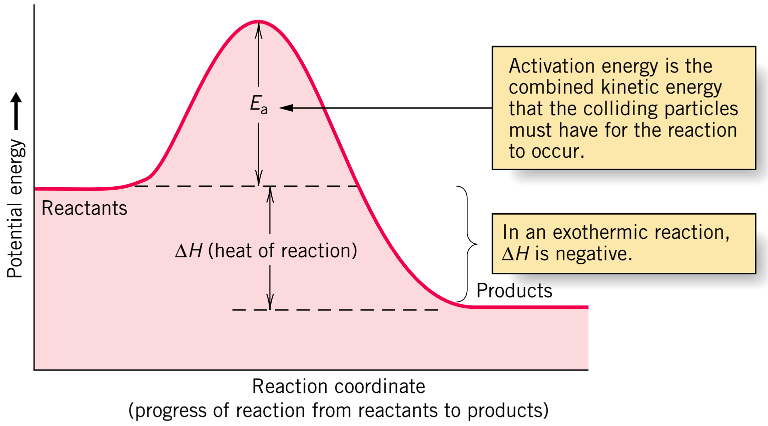
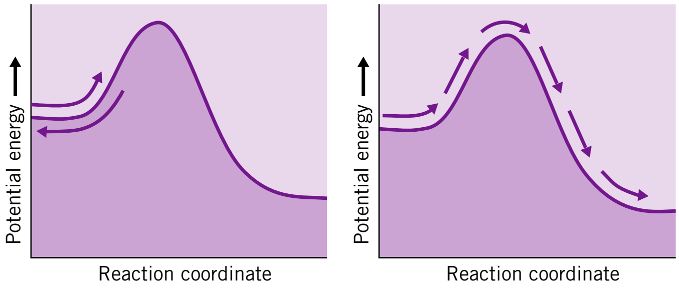

Potential energy
E_a
Activation energy is the combined kinetic energy that the colliding particles must have for the reaction to occur.
Reactants
ΔH (heat of reaction)
In an exothermic reaction, ΔH is negative.
Products
Reaction coordinate
(progress of reaction from reactants to products)

Figure 14.12 | **Potential energy diagram for an exothermic reaction.**



(*a*) An unsuccessful collision; the colliding molecules separate unchanged.

(*b*) A successful collision; the activation energy barrier is crossed and the products are formed.

Figure 14.13 | **The difference between an unsuccessful and a successful collision.**

We can use a potential energy diagram to follow the progress of both an unsuccessful and a successful collision (see Figure 14.13). As two reactant molecules collide, we say that they begin to climb the potential energy barrier as they slow down and experience the conversion of their kinetic energy into potential energy. However, if their combined initial kinetic energies are less than E_a, the molecules are unable to reach the top of the hill (Figure 14.13*a*). Instead, they fall back toward the reactants. They bounce apart, chemically unchanged, with their original total kinetic energy; no net reaction has occurred. On the other hand, if the combined kinetic energy of the colliding molecules equals or exceeds E_a, and if the molecules are oriented properly, they are able to pass over the activation energy barrier and form product molecules (Figure 14.13*b*).

Potential Energy Diagrams and Heat of Reaction

A reaction's potential energy diagram, such as that of Figure 14.12, helps us to visualize the *heat of reaction*, ΔH, a concept introduced in Chapter 7. It's the difference between the potential energy of the products and the potential energy of the reactants. Figure 14.12 shows the potential energy diagram for an *exothermic* reaction because the products have a *lower* potential energy than the reactants. In such a system, the net decrease in potential energy appears as an increase in the molecular kinetic energy of the emerging product molecules. The temperature of the system increases during an exothermic reaction because the average molecular kinetic energy of the system increases.

A potential energy diagram for an endothermic reaction is shown in Figure 14.14. Now, the products have a *higher* potential energy than the reactants and, in terms of the heat of reaction, a net input of energy is needed to form the products. Endothermic reactions produce a cooling effect as they proceed because there is a net conversion of molecular kinetic energy to potential energy. As the *total* molecular kinetic energy decreases, the *average* molecular kinetic energy decreases as well, and the temperature drops.

Notice that E_a for an endothermic process is greater than the heat of reaction. If ΔH is both positive and *high*, E_a must also be high, making such reactions very slow. However, for an exothermic reaction (ΔH is negative), we cannot tell from ΔH how large E_a is. It could be high, making for a slow reaction, despite its being exothermic. If E_a is low, the reaction would be rapid and all its heat would appear quickly.

In Chapter 7, we saw that when the direction of a reaction is reversed, the sign given to the enthalpy change, ΔH, is reversed. In other words, a reaction that is exothermic in the forward direction *must* be endothermic in the reverse direction, and vice versa. This might seem to suggest that reactions are generally reversible. Many are, but if we look again at the energy diagram for a reaction that is exothermic in the forward direction

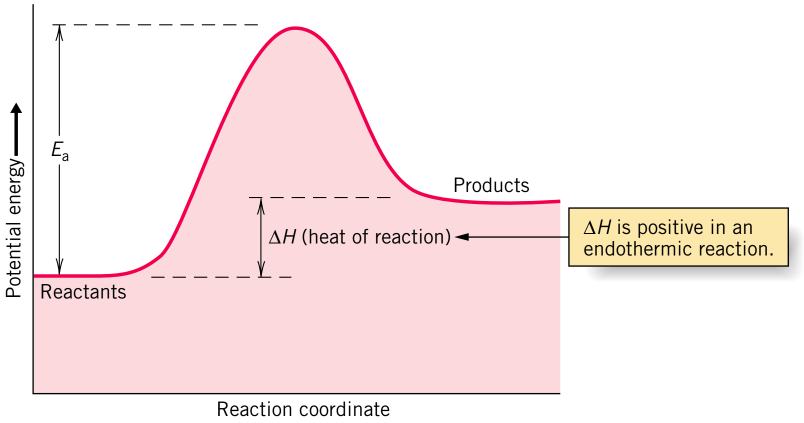
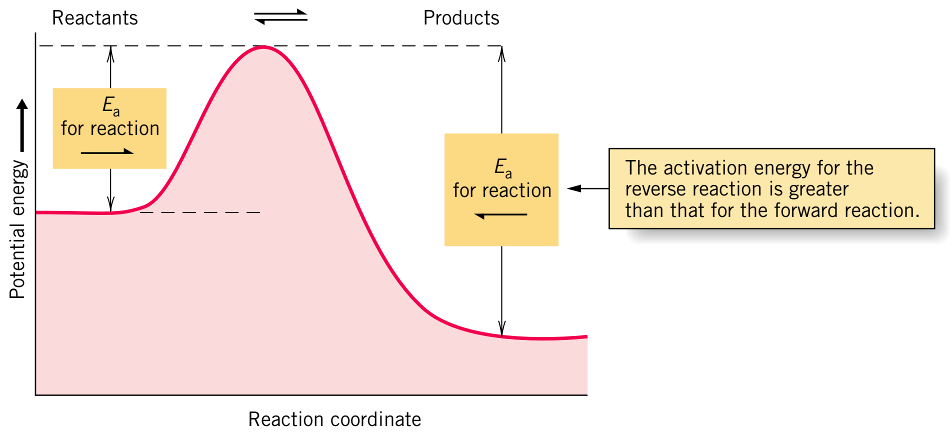

Potential energy
E_a
Products
ΔH (heat of reaction)
ΔH is positive in an endothermic reaction.
Reactants
Reaction coordinate

Figure 14.14 | **A potential energy diagram for an endothermic reaction.**



The activation energy for the reverse reaction is greater than that for the forward reaction.

Figure 14.15 | **The activation energy barrier for the forward and reverse reactions.**

(Figure 14.12), we see that the reaction is endothermic in the opposite direction *and must have a significantly higher activation energy* than the forward reaction. What differs most for the forward and reverse directions is the relative height of the activation energy barrier (Figure 14.15).

One of the main reasons for studying activation energies is that they provide information about what actually occurs during an effective collision. For example, in Figure 14.9*b* on page 665, we described a way that NO_2Cl could react successfully with a Cl atom during a collision. During this collision, there is a moment when the N—Cl bond is partially broken and the new Cl—Cl bond is partially formed. This brief moment during a successful collision is called the reaction's **transition state**. The potential energy of the transition state corresponds to the high point on the potential energy diagram (see Figure 14.16). The unstable chemical species that momentarily exists at this instant, $O_2N \cdots Cl \cdots Cl$, with its partially formed and partially broken bonds, is called the **activated complex**.

The size of the activation energy tells us about the relative importance of bond breaking and bond making during the formation of the activated complex. A very high activation energy suggests, for instance, that bond *breaking* contributes very heavily to the formation of the activated complex because bond breaking is an energy-absorbing process. On the other hand, a low activation energy may mean that bonds of about equal strength are being both broken and formed simultaneously.

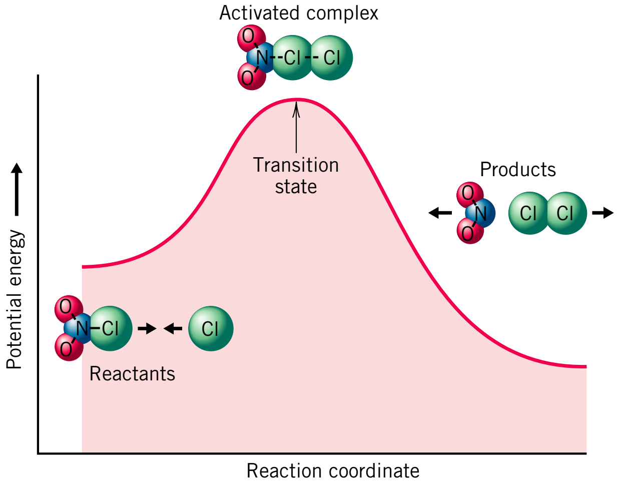


Figure 14.16 | **The transition state and the activated complex.** Formation of an activated complex in the reaction between NO_2Cl and Cl.

$$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$$

14.7 | Activation Energies

We've noted that the activation energy is a useful quantity to know because its value can provide clues to the relative importance of bond breaking and bond making during the formation of the activated complex. The value of E_a can be determined by observing how temperature affects the value of the rate constant, k.

The activation energy is linked to the rate constant by a relationship discovered in 1889 by Svante Arrhenius, whose name you may recall from our discussion of electrolytes and acids and bases in Chapter 5. The usual form of the **Arrhenius equation** is

TOOLS

Arrhenius equation

$$\boxed{k = A\, e^{-E_a/RT}} \tag{14.13}$$

where k is the rate constant, e is the base of the natural logarithm system, and T is the Kelvin temperature. A is a proportionality constant sometimes called the **frequency factor** or the **pre-exponential factor**. R is the gas constant, which we'll express in our study of kinetics in energy units—namely, R equals 8.314 J mol^{-1} K^{-1}.[8]

Graphical Determination of Activation Energy

Equation 14.13 is normally used in its logarithmic form. If we take the natural logarithm of both sides, we obtain

$$\ln k = \ln A - E_a/RT$$

Let's rewrite the equation as

$$\ln k = \ln A - (E_a/R) \times (1/T) \tag{14.14}$$

We know that the rate constant k varies with the temperature T, which also means that the quantity $\ln k$ varies with the quantity $(1/T)$. These two quantities—namely, $\ln k$ and $1/T$—are variables, so Equation 14.14 is in the form of an equation for a straight line:

$$\begin{array}{ccccccc} \ln k & = & \ln A & + & (-E_a/R) & \times & (1/T) \\ \updownarrow & & \updownarrow & & \updownarrow & & \updownarrow \\ y & = & b & + & m & & x \end{array}$$

To determine the activation energy, we can make a graph of $\ln k$ versus $1/T$, measure the slope of the line, and then use the relationship,

$$\text{slope} = -E_a/R$$

to calculate E_a. Example 14.12 illustrates how this is done.

Example 14.12
Determining Energy of Activation Graphically

Consider again the decomposition of NO_2 into NO and O_2. The balanced chemical equation is

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

The following data were collected for the reaction:

Rate Constant, k (L mol^{-1} s^{-1})	Temperature (°C)
7.8	405
9.9	415
14	425
18	435
24	445

---

[8] The units of R given here are actually SI units—namely, the joule (J), the mole (n), and the kelvin (K). To calculate R in these units we need to go back to the defining equation for the universal gas law:

$$R = PV/nT$$

In Chapter 11 we learned that the standard conditions of pressure and temperature are 1 atm and 273.15 K; we expressed the standard molar volume in liters—namely, 22.414 L. But 1 atm equals 1.01325×10^5 N m^{-2}, where N is the SI unit of force, the newton, and m is the meter, the SI unit of length. Thus, m^2 is area given in SI units. From Chapter 11, the ratio of force to area given by N m^{-2} is called the pascal, Pa, and force times distance (i.e., N m) defines one unit of energy in the SI and is called the joule, J. In the SI, volume must be expressed as m^3, to employ the SI unit of length to define volume, and 1 L equals 10^{-3} m^3. We can now calculate R in SI units:

$$R = \frac{(1.01325 \times 10^5\ \text{N m}^{-2}) \times (22.414 \times 10^{-3}\ \text{m}^3)}{(1\ \text{mol} \times 273.15\ \text{K})}$$
$$= 8.314\ \text{N m mol}^{-1}\ \text{K}^{-1} = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Use the graphical method to determine the activation energy for the reaction in kilojoules per mole.

Analysis: We are asked to plot the given rate constants at different temperatures to determine the activation energy for the reaction from the slope of the graph, which is $-E_a/R$.

Assembling the Tools: Equation 14.14 is the tool that applies, but the use of rate data to determine the activation energy graphically requires that we plot ln k, not k, versus the *reciprocal* of the *Kelvin* temperature, so we have to convert the given data into ln k and $1/T$ before we can construct the graph.

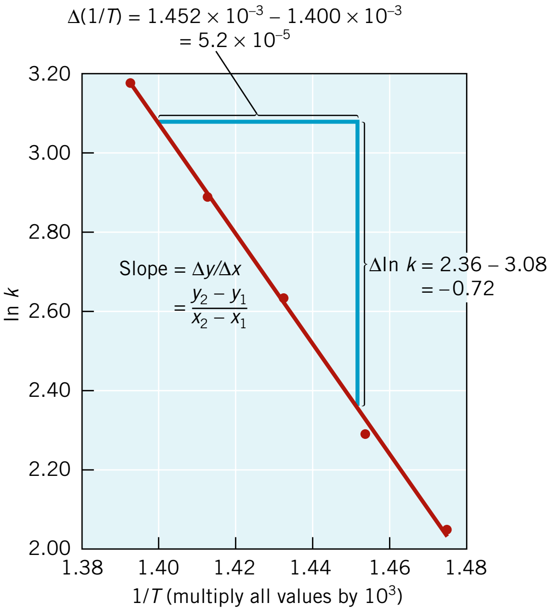
Solution: To illustrate, using the first set of data, the conversions are

$$\ln k = \ln(7.8) = 2.05$$

$$\frac{1}{T} = \frac{1}{(405 + 273)\ \text{K}} = \frac{1}{678\ \text{K}}$$
$$= 1.475 \times 10^{-3}\ \text{K}^{-1}$$

We are carrying extra "significant figures" for the purpose of graphing the data. The remaining conversions give the table in the margin. Then we plot ln k versus $1/T$ as shown in the following figure:

ln k	$1/T$ (K^{-1})
2.05	1.475×10^{-3}
2.29	1.453×10^{-3}
2.64	1.433×10^{-3}
2.89	1.412×10^{-3}
3.18	1.393×10^{-3}



The slope of the curve is obtained as the ratio

$$\text{slope} = \frac{\Delta(\ln k)}{\Delta(1/T)}$$
$$= \frac{-0.72}{5.2 \times 10^{-5}\ \text{K}^{-1}}$$
$$= -1.4 \times 10^{4}\ \text{K} = -E_a/R$$

After changing signs and solving for E_a we have

$$E_a = (8.314\ \text{J mol}^{-1}\ \cancel{\text{K}^{-1}})(1.4 \times 10^{4}\ \cancel{\text{K}})$$
$$= 1.2 \times 105\ \text{J mol}^{-1}$$
$$= 1.2 \times 102\ \text{kJ mol}^{-1}$$

Is the Answer Reasonable? Activation energies must always have a positive sign, and our result is positive. In addition, a check of the units shows that they cancel to give us the correct kJ mol^{-1}. We could try a different pair of points on the same graph to check our work.

Calculating Activation Energies from Rate Constants at Two Temperatures

If the activation energy and the rate constant at a particular temperature are known, the rate constant at another temperature can be calculated using the following relationship, which can be derived from Equation 14.14:

Arrhenius equation, alternate form

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{14.15}$$

This equation can also be used to calculate the activation energy from rate constants measured at two different temperatures. However, the graphical method discussed previously gives more precise values of E_a since more data points are used to plot the graph.

Example 14.13

Calculating the Rate Constant at a Particular Temperature

The reaction $2NO_2 \longrightarrow 2NO + O_2$ has an activation energy of 111 kJ/mol. At 385 °C, $k = 4.9$ L mol^{-1} s^{-1}. What is the value of k at 465 °C?

Analysis: We know the activation energy and k at one temperature and are asked for the value of k at a second temperature.

Assembling the Tools: We will need to use Equation 14.15 as our tool to obtain k at the other temperature. Since the logarithm term contains the ratio of the rate constants, we will solve for the value of this ratio, substitute the known value of k, and then solve for the unknown k.

Solution: Let's begin by writing Equation 14.15:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Organizing the data gives us the following table:

	k (L mol^{-1} s^{-1})	T (K)
1	4.9	385 + 273 = 658 K
2	?	465 + 273 = 738 K

We must use $R = 8.314$ J mol^{-1} K^{-1} and express E_a in joules ($E_a = 1.11 \times 10^5$ J mol^{-1}). Next, we substitute values into the right side of the equation and solve for $\ln(k_2/k_1)$:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-1.11\times10^5\ \cancel{\text{J mol}^{-1}}}{8.314\ \cancel{\text{J mol}^{-1}}\ \text{K}^{-1}}\left(\frac{1}{738\ \text{K}} - \frac{1}{658\ \text{K}}\right)$$

$$= (-1.34\times10^4\ \cancel{\text{K}})(-1.64\times10^{-4}\ \cancel{\text{K}^{-1}})$$

Therefore,

$$\ln\left(\frac{k_2}{k_1}\right) = 2.21$$

Taking the antilog gives the ratio of k_2 to k_1:

$$\frac{k_2}{k_1} = e^{2.21} = 9.09$$

Solving for k_2,

$$k_2 = 9.09\ k_1$$

Substituting the value of k_1 from the data table gives

$$\begin{aligned} k_2 &= 9.09(4.9 \text{ L mol}^{-1} \text{ s}^{-1}) \\ &= 45 \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Is the Answer Reasonable? Although no simple check exists, we have at least found that the value of k for the higher temperature is greater than it is for the lower temperature, as it should be.

Practice Exercises

14.26 | The rate constant is directly proportional to the reaction rate if the same reactant concentrations are used. When determining the stability of a consumer product, less than 5% should decompose in two years at 25 °C. What temperature should we set our oven to if we want to see that same 5% decomposition in one week? Assume the activation energy was previously determined to be 154 kJ mol^{-1}. (*Hint:* All of the information is here to solve the Arrhenius equation.)

14.27 | The reaction $CH_3I + HI \longrightarrow CH_4 + I_2$ was observed to have rate constants $k = 3.2$ L mol^{-1} s^{-1} at 355 °C and $k = 23$ L mol^{-1} s^{-1} at 405 °C. (a) What is the value of E_a expressed in kJ/mol? (b) What would be the rate constant at 310 °C?

14.28 | Ozone decomposes to form oxygen molecules and oxygen atoms, $O_3(g) \longrightarrow O_2(g) + O(g)$, in the upper atmosphere. The energy of activation for this reaction is 93.1 kJ/mol. At 600 K, the rate constant for this reaction is $3.37 \times 10^3\ M^{-1}\ \text{s}^{-1}$. At what temperature will the rate constant be ten times larger, or $3.37 \times 10^4\ M^{-1}\ \text{s}^{-1}$?

Analyzing and Solving Multi-Concept Problems

A pressure cooker decreases the amount of time it takes to cook food. It does so by sealing the pot and using the water vapor to increase the pressure in the pot; this, in turn, increases the temperature at which water boils (see the vapor pressure graph of water in Chapter 12, page 545). Because cooking involves chemical processes, food cooks faster at higher temperatures. Often, the pressure inside a pressure cooker increases to 2.0 atm. How long will it take to cook 1.0 pound of beans in a pressure cooker if it takes 55 minutes to cook them in boiling water at 1 atm? The pressure in the unsealed pot is 1.0 atm and the boiling point is 100 °C. We will assume that we are using a 4.0 liter pot and that the number of moles of gas in the pot increases from 0.13 mol to 0.25 mol, and that $E_a = 1.77 \times 10^5$ J mol^{-1} K^{-1}. In addition, since the cooking occurs in the liquid and the beans are covered in water, the reactant concentrations will not change, so the rate constant is directly proportional to the reaction rate.

Analysis We are asked for the amount of time it takes to cook 1.0 pound of beans in a pressure cooker at a higher temperature than at the normal boiling point of water. Since we are looking for a rate that is related to temperature, we can use the Arrhenius equation. We need to decide which form of the Arrhenius equation to use. We are given a time for cooking, 55 min/lb, but that is not a rate or a rate constant, so we will have to convert it into a rate and use the fact that the reaction rates are directly proportional to the rate constants, since the concentrations of the reactions are not changing. We also have the temperature, 100 °C for the unpressurized reaction, as well as the activation energy for the process, so we can use Equation 14.15 to find the rate at the higher temperature. In place of the ratio of the rate constants, we can use the rates, because they are directly proportional to each other.

Unfortunately, we are not given the higher temperature, so we will need to calculate it first. We are given a volume and the number of moles of gas, which leads us to the ideal gas law. Using the ideal gas law, $PV = nRT$, we can calculate the temperature of the gas at the higher pressure.

Now, we have one rate, the two temperatures, and the energy of activation. We can find the other rate. The three steps that we will have to carry out are (1) finding the temperature of the pressure cooker, (2) determining the rate of the reaction under atmospheric pressure, and (3) finding the rate of cooking at the higher temperature using the Arrhenius equation and then determining how long it will take to cook the beans.

PART 1

Assembling the Tools We will use the ideal gas law ($PV = nRT$) as our first tool to find the temperature of the pressure cooker.

Solution Let us start by assembling the data we will need:

Pressure: $P = 2.0$ atm Volume: $V = 4.0$ L

Number of moles: $n = 0.25$ mol Gas constant: $R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

Now we can rearrange the equation to see how temperature is related to the rest of the equation:

$$\begin{aligned} PV &= nRT \\ T &= \frac{PV}{nR} \end{aligned}$$

We can substitute these values into the equation to arrive at the higher temperature:

$$\begin{aligned} T &= \frac{(2.0\ \cancel{\text{atm}})(4.0\ \cancel{\text{L}})}{(0.25\ \cancel{\text{mol}})(0.0821\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \text{K}^{-1})} \\ T &= 390\ \text{K} \end{aligned}$$

PART 2

Assembling the Tools We have the amount of time to cook the beans at 100 °C, 55 min/lb, and we need to have a rate for that. If we take the inverse of the time, we will get the amount cooked per minute.

Solution

$$\begin{aligned} \text{rate} &= \frac{1.0\ \text{lb}}{55\ \text{min}} \\ \text{rate} &= 0.0182\ \text{lb min}^{-1} \end{aligned}$$

PART 3

Assembling the Tools We have the two temperatures, the rate for the slow reaction, and the energy of activation. For this step, the tool we can use is the Arrhenius equation, Equation 14.15:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solution We can have k_2 as the rate we are looking for, and set up the rest of the data as follows:

$E_a = 1.77 \times 10^5\ \text{J mol}^{-1}$

$R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$T_1 = 373$ K rate$_1 = 0.0182$ lb/min

$T_2 = 390$ K rate$_2 = ?$

Substituting these values into the equation gives us

$$\ln\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = -\left(\frac{1.77\times10^5\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}\ \text{K}^{-1}}\right)\left(\frac{1}{390\ \text{K}}-\frac{1}{373\ \text{K}}\right)$$

$$\ln\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = -(1.64\times10^5\text{K})(2.56\times10^{-3}\ \text{K}^{-1} - 2.68\times10^{-3}\ \text{K}^{-1})$$

$$\ln\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = -(1.64\times10^5\ \cancel{\text{K}})(-1.17\times10^{-4}\ \cancel{\text{K}^{-1}})$$

$$\ln\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = 2.49$$

$$\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = e^{2.49}$$

$$\frac{\text{rate}_2}{0.0182\ \text{lb/min}} = 12$$

$$\text{rate}_2 = 0.22\ \text{lb/min}$$

Finally, we want to know how many minutes it takes to cook 1.0 lb of beans in the pressure cooker, so we need to take the inverse of the value for rate_2 and multiply by 1.0 lb:

$$\text{time} = \frac{1\ \text{min}}{0.22\ \text{lb}} \times 1.0\ \text{lb}$$

$$\text{time} = 4.5\ \text{min, or about 5 minutes}$$

■ Are the Answers Reasonable? One check is to look at the reasoning. Does the rate of the reaction go up if the temperature goes up? Another way to ask the question is: Does the time it takes to cook the beans go down? Both answers are "yes," so we are on the right track. Next, is the amount of time reasonable? Five minutes to cook something is reasonable, as long as the temperature is high enough.

14.8 | Mechanisms of Reactions

A balanced equation generally describes only a net overall change. Usually, however, the net change is the result of a series of simple reactions that are not at all evident from the equation. Consider, for example, the combustion of propane, C_3H_8:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

Anyone who has ever played billiards knows that this reaction simply cannot occur in a single, simultaneous collision between one propane molecule and five oxygen molecules. Just getting only three balls to come together with but one "click" on a flat, two-dimensional surface is extremely improbable. How unlikely it must be, then, for the *simultaneous* collision in three-dimensional space of six reactant molecules, one of which must be C_3H_8 and the other five O_2. Instead, the combustion of propane proceeds very rapidly by a series of much more probable steps. *The series of individual steps that add up to the overall observed reaction is called the* **reaction mechanism**. Information about reaction mechanisms is one of the dividends paid by the study of reaction rates.

Each individual step in a reaction mechanism is a simple chemical reaction called an *elementary process*. An **elementary process** is a reaction involving collisions between molecules. As you will soon see, a rate law can be written from the equation for an elementary process, using coefficients as exponents for the concentration terms without requiring experiments to determine the exponents. For most reactions, the individual elementary processes cannot actually be observed because they involve substances of fleeting existence; instead, we only see the net reaction. Therefore, the mechanism a chemist writes is really a *theory* about what occurs step-by-step as the reactants are changed to the products.

Because the individual steps in a mechanism usually cannot be observed directly, devising a mechanism for a reaction requires some ingenuity. However, we can immediately tell whether a proposed mechanism is feasible, because *the rate law derived from the mechanism must agree with the experimental rate law for the reaction.*

Elementary Processes

Consider the following elementary process that involves collisions between two identical molecules, leading directly to the products shown:

$$2NO_2 \longrightarrow NO_3 + NO \qquad \textbf{(14.16)}$$

$$\text{Rate} = k\,[NO_2]^x$$

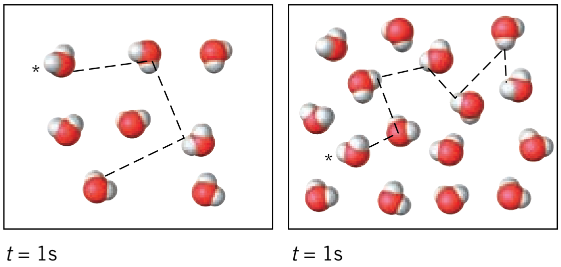


Figure 14.17 | **The relative number of collisions in a given amount of time.** For the molecule marked with an asterisk, *, the number of collisions in a given amount of time doubles when the concentration doubles. Since there are now twice as many molecules, each one has twice as many collisions.

How can we predict the value of the exponent, x? Suppose the NO_2 concentration were doubled. There would now be *twice* as many NO_2 molecules and *each* would have *twice* as many neighbors with which to collide (Figure 14.17). The number of NO_2-to-NO_2 collisions per second would doubly double—in other words, increase by a factor of 4. This would cause the rate to increase by a factor of 4, which is 2^2. Earlier we saw that when doubling a concentration leads to a four-fold increase in the rate, the concentration of that reactant is raised to the second power in the rate law. Thus, if Equation 14.16 represents an elementary process, its rate law should be

$$\text{rate} = k\,[NO_2]^2$$

Notice that the exponent in the rate law for this elementary process is the same as the coefficient in the chemical equation. Similar analyses for other types of elementary processes lead to similar observations and the following statement:

TOOLS

Rate laws for elementary processes

> The exponents in the rate law for an elementary process are equal to the coefficients of the reactants in the chemical equation for that elementary process.

Remember that this rule applies only to *elementary processes*. If all we know is the balanced chemical equation for the overall reaction, the only way we can find the exponents of the rate law is by doing experiments.

Rate Laws and Rate-Determining Steps

How does the ability to predict the rate law of an elementary process help chemists predict reaction mechanisms? To answer this question, let's look at two reactions and what are believed to be their mechanisms. (There are many other, more complicated systems, and *Chemistry Outside the Classroom 14.1* describes one type, the free radical chain reaction, that is particularly important.) Let's consider two ways in which mechanisms and experimental rate laws are used.

First Case: First Step as the Rate-Determining Step

First, consider the gaseous reaction,

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2 \qquad \textbf{(14.17)}$$

Experimentally, the rate is first order in NO_2Cl, so the rate law is

$$\text{rate} = k\,[NO_2Cl] \qquad (\textit{experimental})$$

The first question we might ask is, Could the overall reaction (Equation 14.17) occur in a single step by the collision of two NO_2Cl molecules? The answer is "no," because then it would be an elementary process and the rate law predicted for it would include a squared term, $[NO_2Cl]^2$. Instead, the experimental rate law is first order in NO_2Cl. Thus, the predicted and experimental rate laws don't agree, so we must look further to find the mechanism of the reaction.

CHEMISTRY OUTSIDE THE CLASSROOM 14.1

Free Radicals, Explosions, Octane Ratings, and Aging

A **free radical** is a very reactive species that contains one or more unpaired electrons. Examples are chlorine atoms formed when a Cl_2 molecule absorbs a photon (light) of the appropriate energy:

$$Cl_2 + \text{light energy } (h\nu) \longrightarrow 2Cl\cdot$$

(A dot placed next to the symbol of an atom or molecule represents an unpaired electron and indicates that the particle is a free radical.) The reason free radicals are so reactive is because of the tendency of electrons to become paired through the formation of either ions or covalent bonds.

Free radicals are important in many gaseous reactions, including those responsible for the production of photochemical smog in urban areas. Reactions involving free radicals have useful applications, too. For example, many plastics are made by reactions that take place by mechanisms that involve free radicals. In addition, free radicals play a part in *thermal cracking*, one of the most important processes in the petroleum industry. This reaction is used to break C—C and C—H bonds in long-chain hydrocarbons to produce the smaller molecules that give gasoline a higher octane rating. An example is the formation of free radicals in the thermal cracking reaction of butane. When butane is heated to 700–800 °C, one of the major reactions that occurs is

$$CH_3—CH_2 : CH_2—CH_3 \xrightarrow{\text{heat}} CH_3CH_2\cdot + CH_3CH_2\cdot$$

The central C—C bond of butane is shown here as a pair of dots, **:**, rather than the usual dash. When the bond is broken, the electron pair is divided between the two free radicals that are formed. This reaction produces two ethyl radicals, $CH_3CH_2\cdot$.

Free radical reactions tend to have high initial activation energies because chemical bonds must be broken to form the radicals. Once the free radicals are formed, however, reactions in which they are involved tend to be very rapid.

Free Radical Chain Reactions

In many cases, a free radical reacts with a reactant molecule to give a product molecule plus another free radical. Reactions that involve such a step are called **chain reactions**.

Many explosive reactions are chain reactions involving free radical mechanisms. One of the most studied reactions of this type is the formation of water from hydrogen and oxygen. The elementary processes involved can be described according to their roles in the mechanism.

The reaction begins with an **initiation step** that gives free radicals:

$$H_2 + O_2 \xrightarrow{\text{hot surface}} 2OH\cdot \qquad \text{(initiation)}$$

The chain continues with a **propagation step**, which produces the product plus another free radical.

$$OH\cdot + H_2 \longrightarrow H_2O + H\cdot \qquad \text{(propagation)}$$

The reaction of H_2 and O_2 is explosive because the mechanism also contains **branching steps**:

$$\left.\begin{array}{l} H\cdot + O_2 \longrightarrow OH\cdot + O\cdot \\ O\cdot + H_2 \longrightarrow OH\cdot + H\cdot \end{array}\right] \quad \text{(branching)}$$

Thus, the reaction of one H· with O_2 leads to the net production of two OH· plus an O·. Every time an H· reacts with oxygen, then, there is an increase in the number of free radicals in the system. The free radical concentration grows rapidly, and the reaction rate becomes explosively fast.

Chain mechanisms also contain **termination steps**, which remove free radicals from the system. In the reaction of H_2 and O_2, the wall of the reaction vessel serves to remove H·, which tends to halt the chain process.

$$2H\cdot \xrightarrow{\text{wall}} H_2$$

Free Radicals and Aging

Direct experimental evidence also exists for the presence of free radicals in functioning biological systems. These highly reactive species play many roles, but one of the most interesting is their apparent involvement in the aging process. One theory suggests that free radicals attack protein molecules in collagen. Collagen is composed of long strands of proteins and is found throughout the body, especially in the flexible tissues of the lungs, skin, muscles, and blood vessels. Attack by free radicals seems to lead to cross-linking between these fibers, which makes them less flexible. The most readily observable result of this is the stiffening and hardening of the skin that accompanies aging or too much sunbathing (see Figure 1).

Free radicals also seem to affect fats (lipids) within the body by promoting the oxidation and deactivation of enzymes that are normally involved in the metabolism of lipids. Over a long period, the accumulated damage gradually reduces the efficiency with which the cell carries out its activities. Interestingly, vitamin E appears to be a natural free radical inhibitor. Diets that are deficient in vitamin E produce effects resembling radiation damage and aging.

Still another theory of aging suggests that free radicals attack the DNA in the nuclei of cells. DNA is the substance that is responsible for directing the chemical activities required for the successful functioning of the cell. Reactions with free radicals cause a gradual accumulation of errors in the DNA, which reduce the efficiency of the cell and can lead, ultimately, to malfunction and cell death.

Figure 1 People exposed to sunlight over long periods, like this woman from Nepal (a small country between India and Tibet), tend to develop wrinkles because ultraviolet radiation causes changes in their skin. *(Franck Guiziou/Hemis/© Corbis)*

On the basis of chemical intuition and other information that we won't discuss here, chemists believe the actual mechanism of the reaction in Equation 14.17 is the following two-step sequence of elementary processes:

■ The Cl atom formed here is called a *reactive intermediate.* We never actually observe the Cl because it reacts so quickly.

$$NO_2Cl \longrightarrow NO_2 + Cl$$
$$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$$

Notice that when the two reactions are added, the *intermediate*, Cl, drops out and we obtain the net overall reaction given in Equation 14.17. *Being able to add the elementary processes and thus to obtain the overall reaction is another major test of a mechanism.*

In any multi-step mechanism, one step is usually much slower than the others. In this mechanism, for example, it is believed that the first step is slow and that once a Cl atom forms, it reacts very rapidly with another NO_2Cl molecule to give the final products.

The final products of a multi-step reaction cannot appear faster than the products of the slow step, so the slow step in a mechanism is called the **rate-determining step** or the **rate-limiting step**. In the preceding two-step mechanism, then, the first reaction is the rate-determining step because the final products can't be formed faster than the rate at which Cl atoms form.

The rate-determining step is similar to a slow worker on an assembly line. The production rate depends on how quickly the slow worker works, regardless of how fast the other workers are. The factors that control the speed of the rate-determining step, therefore, also control the overall rate of the reaction. This means that *the rate law for the rate-determining step is directly related to the rate law for the overall reaction.*

Because the rate-determining step is an elementary process, we can predict its rate law from the coefficients of its reactants. The coefficient of NO_2Cl in its relatively slow breakdown to NO_2 and Cl is 1. Therefore, the rate law predicted for the first step is

$$\text{rate} = k\,[NO_2Cl] \qquad (\textit{predicted})$$

Thus, the predicted rate law derived for the two-step mechanism agrees with the experimentally measured rate law. Although this doesn't *prove* that the mechanism is correct, it does provide considerable support for it. From the standpoint of kinetics, therefore, the mechanism is reasonable.

Second Case: Second Step as the Rate-Determining Step

The second reaction mechanism that we will study is that of the following gas phase reaction:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad \textbf{(14.18)}$$

The experimentally determined rate law is

$$\text{rate} = k\,[NO]^2\,[H_2] \qquad (\textit{experimental})$$

Based on this rate law, Equation 14.18 could *not* itself be an elementary process. If it were, the exponent for $[H_2]$ would have to be 2. Instead, a mechanism involving two or more steps must be involved.

A chemically reasonable mechanism that yields the correct form for the rate law consists of the following two steps:

$$2NO + H_2 \longrightarrow N_2O + H_2O \qquad \text{(slow)}$$
$$N_2O + H_2 \longrightarrow N_2 + H_2O \qquad \text{(fast)}$$

One test of the mechanism, as we said, is that the two equations must add to give the correct overall equation; and they do. Furthermore, the chemistry of the second step has actually been observed in separate experiments. N_2O is a known compound, and it does react with H_2 to give N_2 and H_2O. Another test of the mechanism involves the coefficients of NO and H_2 in the predicted rate law for the first step, the supposed rate-determining step:

$$\text{rate} = k\,[NO]^2\,[H_2] \qquad (\textit{predicted})$$

This rate equation does match the experimental rate law, but there is still a serious flaw in the proposed mechanism. If the postulated slow step actually described an elementary process, it would involve the simultaneous collision between three molecules, two NO and one H_2. A three-way collision is so unlikely that if it were really involved in the mechanism, the overall reaction would be extremely slow. Reaction mechanisms seldom include elementary processes that involve more than two-body or **bimolecular collisions.**

Chemists believe the reaction in Equation 14.18 proceeds by the following three-step sequence of bimolecular elementary processes:

$$\begin{aligned} 2NO &\rightleftharpoons N_2O_2 && \text{(fast)} \\ N_2O_2 + H_2 &\longrightarrow N_2O + H_2O && \text{(slow)} \\ N_2O + H_2 &\longrightarrow N_2 + H_2O && \text{(fast)} \end{aligned}$$

In this mechanism, the first step is proposed to be a rapidly established equilibrium in which the unstable intermediate N_2O_2 forms in the forward reaction and then quickly decomposes into NO by the reverse reaction. The rate-determining step is the reaction of N_2O_2 with H_2 to give N_2O and a water molecule. The third step is the reaction mentioned above. Once again, notice that the three steps add to give the net overall change.

Since the second step is rate determining, the rate law for the reaction should match the rate law for this step. We predict this to be

$$\text{rate} = k\,[N_2O_2]\,[H_2] \tag{14.19}$$

■ The occurrence of N_2O_2 as an intermediate in the proposed mechanism can only be surmised. The compound is never present at a detectable concentration because it's too unstable.

However, the experimental rate law does not contain the species N_2O_2. Therefore, we must find a way to express the concentration of N_2O_2 in terms of the reactants in the overall reaction. To do this, let's look closely at the first step of the mechanism, which we view as a reversible reaction.

The rate in the forward direction, in which NO is the reactant, is

$$\text{rate (forward)} = k_f\,[NO]^2$$

The rate of the reverse reaction, in which N_2O_2 is the reactant, is

$$\text{rate (reverse)} = k_r\,[N_2O_2]$$

If we view this as a dynamic equilibrium, then the rate of the forward and reverse reactions are equal, which means that

■ Recall that in a dynamic equilibrium, forward and reverse reactions occur at equal rates.

$$k_f\,[NO]^2 = k_r\,[N_2O_2] \tag{14.20}$$

Since we would like to eliminate N_2O_2 from the rate law in Equation 14.19, let's solve Equation 14.20 for $[N_2O_2]$:

$$[N_2O_2] = \frac{k_f}{k_r}[NO]^2$$

Substituting into the rate law in Equation 14.19 yields

$$\text{rate} = k\left(\frac{k_f}{k_r}\right)[NO]^2[H_2]$$

Combining all of the constants into one (k') gives

$$\text{rate} = k'\,[NO]^2\,[H_2] \qquad (\textit{predicted})$$

■ There are many reactions that do not follow simple first- or second-order rate laws and have mechanisms far more complex than those studied in this section. Even so, their more complex kinetics still serve as clues to their complex set of elementary processes.

Now, the rate law derived from the mechanism matches the rate law obtained experimentally. The three-step mechanism does appear to be reasonable on the basis of kinetics.

The procedure we have worked through here applies to many reactions that proceed by mechanisms involving sequential steps. Steps that precede the rate-determining step are considered to be rapidly established equilibria involving unstable intermediates.

Relating the Proposed Mechanism to the Experimental Rate Law

Although chemists may devise other experiments to help prove or disprove the correctness of a mechanism, one of the strongest pieces of evidence is the experimentally measured rate law for the overall reaction. No matter how reasonable a particular mechanism may appear, if its elementary processes cannot yield a predicted rate law that matches the experimental one, the mechanism is wrong and must be discarded.

In some cases the experimental rate law may suggest two different but equally probable mechanisms. One method for testing mechanisms is to find evidence of unique intermediates. In the previous mechanisms, both had N_2O as an intermediate, but the second mechanism had N_2O_2 as a unique intermediate. If experiments could show the existence of N_2O_2 during the reaction, the second mechanism would have added evidence that it is the correct mechanism.

Practice Exercises

14.29 | Select the reactions below that may be elementary processes. For those not selected, explain why they are not elementary processes.

(a) $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$

(b) $NO + O_3 \longrightarrow NO_2 + O_2$

(c) $2NO + H_2 \longrightarrow N_2O + H_2O$

(d) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

(e) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(f) $3H_2 + N_2 \longrightarrow 2NH_3$

(*Hint:* How many molecules are likely to collide at exactly the same time?)

14.30 | Ozone, O_3, reacts with nitric oxide, NO, to form nitrogen dioxide and oxygen:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

This is one of the reactions involved in the formation of photochemical smog. If this reaction occurs in a single step, what is the expected rate law for the reaction?

14.31 | The mechanism for the decomposition of NO_2Cl is

$$NO_2Cl \rightleftharpoons NO_2 + Cl$$
$$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$$

What would the predicted rate law be if the second step in the mechanism were the rate-determining step?

14.9 | Catalysts

A **catalyst** is a substance that changes the rate of a chemical reaction without itself being used up. In other words, all of the catalyst added at the start of a reaction is present chemically unchanged after the reaction has gone to completion. The action caused by a catalyst is called **catalysis.** Broadly speaking, there are two kinds of catalysts. *Positive catalysts* speed up reactions, whereas *negative catalysts*, usually called *inhibitors,* slow reactions down. After this, when we use “catalyst” we’ll mean positive catalyst, the usual connotation.

Although the catalyst is not part of the overall reaction, it does participate by changing the mechanism of the reaction. The catalyst provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalyzed reaction (see Figure 14.18). Because the activation energy along this new route is lower, a greater fraction of the collisions of the reactant molecules have the minimum energy needed to react, so the reaction proceeds faster.

Catalysts can be divided into two groups—**homogeneous catalysts**, which exist in the same phase as the reactants, and **heterogeneous catalysts**, which exist in a separate phase from the reactants.

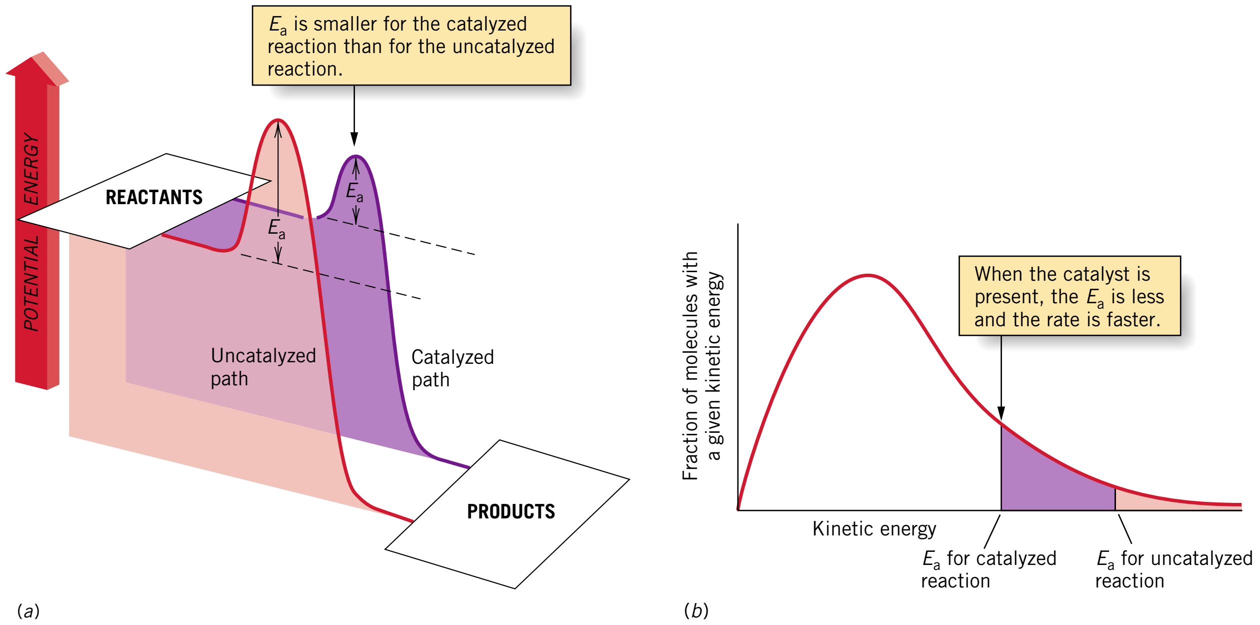

E_a is smaller for the catalyzed reaction than for the uncatalyzed reaction.
POTENTIAL ENERGY
REACTANTS
E_a
E_a
Uncatalyzed path
Catalyzed path
PRODUCTS
(a)
Fraction of molecules with a given kinetic energy
When the catalyst is present, the E_a is less and the rate is faster.
Kinetic energy
E_a for catalyzed reaction
E_a for uncatalyzed reaction
(b)

Figure 14.18 | **The effect of a catalyst on a reaction.** (*a*) The catalyst provides an alternative, low-energy path from the reactants to the products. (*b*) A larger fraction of molecules have sufficient energy to react when the catalyzed path is available.

Homogeneous Catalysts

An example of homogeneous catalysis is found in the now outdated *lead chamber process* for manufacturing sulfuric acid. To make sulfuric acid by this process, sulfur is burned to give SO_2, which is then oxidized to SO_3. The SO_3 is dissolved in water as it forms to give H_2SO_4.

- In the modern process for making sulfuric acid, the contact process, vanadium(V) oxide, V_2O_5, is a heterogeneous catalyst that promotes the oxidation of sulfur dioxide to sulfur trioxide.

$$S + O_2 \longrightarrow SO_2$$
$$SO_2 + \tfrac{1}{2}O_2 \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Unassisted, the second reaction, the oxidation of SO_2 to SO_3, occurs slowly. In the lead chamber process, the SO_2 is combined with a mixture of NO, NO_2, air, and steam in large, lead-lined reaction chambers. The NO_2 readily oxidizes the SO_2 to give NO and SO_3. The NO is then reoxidized to NO_2 by oxygen.

- The NO_2 is regenerated in the second reaction and so is recycled over and over. Thus, only small amounts of it are needed in the reaction mixture to do an effective catalytic job.

$$NO_2 + SO_2 \longrightarrow NO + SO_3$$
$$NO + \tfrac{1}{2}O_2 \longrightarrow NO_2$$

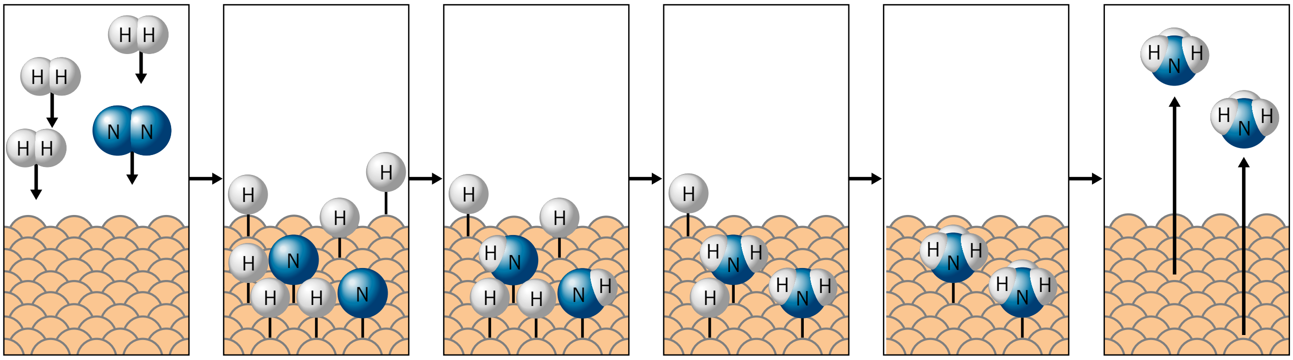
The NO_2 serves as a catalyst by being an oxygen carrier and by providing a low-energy path for the oxidation of SO_2 to SO_3. Notice that the NO_2 is regenerated; it has not been permanently changed, a necessary condition for any catalyst.

Heterogeneous Catalysts

A heterogeneous catalyst is commonly a solid, and it usually functions by promoting a reaction on its surface. One or more of the reactant molecules are adsorbed onto the surface of the catalyst, where an interaction with the surface increases their reactivity. An example is the synthesis of ammonia from hydrogen and nitrogen by the Haber process.

- **Adsorption** means that molecules bind to a surface.

$$3H_2 + N_2 \longrightarrow 2NH_3$$



Molecules of H_2 and N_2 approach the iron atoms (bottom) on the surface of the catalyst.

Molecules of H_2 and N_2 dissociate into atoms.

Bonds from H to N begin to form.

Bond formation continues.

Ammonia molecules have formed.

Ammonia molecules leave the catalyst's surface.

Figure 14.19 | **The Haber process.** Catalytic formation of ammonia molecules from hydrogen and nitrogen on the surface of a catalyst.

The reaction takes place on the surface of an iron catalyst that contains traces of aluminum and potassium oxides. It is thought that hydrogen molecules and nitrogen molecules dissociate while being held on the catalytic surface. The hydrogen atoms then combine with the nitrogen atoms to form ammonia. Finally, the completed ammonia molecule breaks away, freeing the surface of the catalyst for further reaction. This sequence of steps is illustrated in Figure 14.19.

Heterogeneous catalysts are used in many important commercial processes. The petroleum industry uses heterogeneous catalysts to crack hydrocarbons into smaller fragments and then re-form them into the useful components of gasoline (see Figure 14.20). The availability of such catalysts allows refineries to produce gasoline, jet fuel, or heating oil from crude oil in any ratio necessary to meet the demands of the marketplace.

A vehicle that uses unleaded gasoline is equipped with a catalytic converter (Figure 14.21) designed to lower the concentrations of exhaust gas pollutants, such as carbon monoxide, unburned hydrocarbons, and nitrogen oxides. The catalysts are nanometer-sized particles of platinum, ruthenium, and rhodium dispersed in a honeycomb of a high-temperature ceramic. The large ratio of surface area to mass enables the catalytic converter to react with

(*a*) (*b*)

Figure 14.20 | **Catalysts are very important in the petroleum industry.** (*a*) Catalytic cracking towers at an oil refinery. (*b*) A variety of catalysts are available as beads, powders, or in other forms for various refinery operations. *(a: Wes Thompson/© Corbis; b: BASF Corporation)* large volumes of exhaust efficiently. Air is introduced into the exhaust stream that then passes over a catalyst that adsorbs CO, NO, and O_2. The NO dissociates into N and O atoms, and the O_2 also dissociates into atoms. Pairing of nitrogen atoms then produces N_2, and the oxidation of CO by oxygen atoms produces CO_2. Unburned hydrocarbons are also oxidized to CO_2 and H_2O. The catalysts in catalytic converters are deactivated or "poisoned" by lead-based octane boosters like tetraethyl lead $[Pb(C_2H_5)_4]$. Leaded gasoline was finally banned in 1995. Leaded gasoline also posed an environmental hazard from the lead emitted in automobile exhaust.

The poisoning of catalysts is also a major problem in many industrial processes. Methyl alcohol (methanol, CH_3OH), for example, is a promising fuel that can be made from coal and steam by the reaction

$$\text{C (from coal)} + H_2O \longrightarrow CO + H_2$$

followed by

$$CO + 2H_2 \longrightarrow CH_3OH$$

A catalyst for the second step is copper(I) ion held in solid solution with zinc oxide. However, traces of sulfur, a contaminant in coal, must be avoided because sulfur reacts with the catalyst and destroys its catalytic activity.

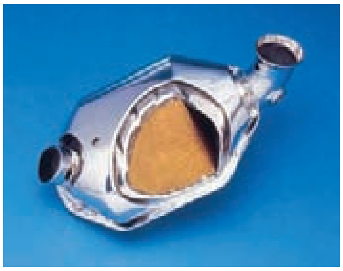


Figure 14.21 | **A modern catalytic converter of the type used in about 80% of new cars.** Part of the converter has been cut away to reveal the porous ceramic material that serves as the support for the catalyst. *(Courtesy BASF Corporation)*

Enzymes

In living systems, complex protein-based molecules called *enzymes* catalyze almost every reaction that occurs in living cells. Enzymes contain a specially shaped area called an "active site" that lowers the energy of the transition state of the reaction being catalyzed. This causes the reaction rate to increase significantly. Many poisons have been shown to work by blocking important enzyme systems. Heavy metals bind to sulfur-containing groups and distort the active site. Many modern drugs work by inhibiting the catalytic activity of specific enzymes in the human body. In the pharmaceutical industry, chemists use molecular modeling to design drug molecules that have optimum shapes to fit enzymatic active sites. The better the fit, the more potent the drug will be.

Summary

Reaction Rates. The speeds or **rates** of reactions are controlled by five factors: (1) the nature of the reactants, (2) the ability of the reactants to meet, (3) the concentrations of the reactants, (4) the temperature, and (5) the presence of catalysts. The rates of **heterogeneous reactions** are determined largely by the area of contact between the phases; the rates of **homogeneous reactions** are determined by the concentrations of the reactants. The rate is measured by monitoring the change in reactant or product concentrations with time:

$$\text{Rate} = \Delta(\text{concentration})/\Delta(\text{time})$$

In any chemical reaction, the rates of formation of products and the rates of disappearance of reactants are related by the coefficients of the balanced overall chemical equation.

Rate Laws. The **rate law** for a reaction relates the reaction rate to the molar concentrations of the reactants. The rate is proportional to the product of the molar concentrations of the reactants, each raised to an appropriate power. These exponents must be determined by experiments in which the concentrations are varied and the effects of the variations on the rate are measured. The proportionality constant, $\boldsymbol{k}$, is called the **rate constant**. Its value depends on temperature but not on the concentrations of the reactants. The sum of the exponents in the rate law is the **order** (or overall order) of the reaction.

Concentration and Time. Equations exist that relate the concentration of a reactant at a given time t to the initial concentration and the rate constant. The time required for half of a reactant to disappear is the **half-life**, $\boldsymbol{t_{1/2}}$. For a first-order reaction, the half-life is a constant that depends only on the rate constant for the reaction; it is independent of the initial concentration. The half-life for a second-order reaction is inversely proportional both to the initial concentration of the reactant and to the rate constant. The half-life for a zero-order reaction is inversely proportional to the rate constant and proportional to the inital concentration.

Theories of Reaction Rate. According to **collision theory**, the rate of a reaction depends on the number of **effective collisions** per second of the reactant particles, which is only an extremely small fraction of the total number of collisions per second. This fraction is so small partly because the reactant molecules must be suitably oriented, but mostly because the colliding molecules must jointly possess a minimum molecular kinetic energy called the **activation energy**, E_a. As the temperature increases, a larger fraction of the collisions has this necessary energy, making more collisions effective each second and the reaction faster.

Transition state theory visualizes how the energies of molecules and the orientations of their nuclei interact as they collide. In this theory, the energy of activation is viewed as an energy barrier on the reaction's potential energy diagram. The *heat of reaction* is the net potential energy difference between the reactants and the products. In reversible reactions, the values of E_a for both the forward and reverse reactions can be identified on an energy diagram. The species at the high point on an energy diagram is the **activated complex** and is said to be in the **transition state**.

Determining the Activation Energy. **The Arrhenius equation** lets us see how changes in activation energy and temperature affect a rate constant. The Arrhenius equation also lets us determine E_a either graphically or by a calculation using the appropriate form of the equation. The calculation requires two rate constants determined at two temperatures. The graphical method uses more values of rate constants at more temperatures and thus usually yields more accurate results. The activation energy and the rate constant at one temperature can be used to calculate the rate constant at another temperature.

Reaction Mechanisms. The detailed sequence of elementary processes that lead to the net chemical change is the **mechanism** of the reaction. Since intermediates usually cannot be detected, the mechanism is a theory. Support for a mechanism comes from matching the predicted rate law for the mechanism with the rate law obtained from experimental data. For the **rate-determining step** or for any **elementary process**, the corresponding rate law has exponents equal to the coefficients in the balanced chemical equation for the elementary process.

Catalysts. **Catalysts** are substances that change a reaction rate but are not used up by the reaction. Negative catalysts inhibit reactions. Positive catalysts provide alternative paths for reactions for which at least one step has a smaller activation energy than the uncatalyzed reaction. **Homogeneous catalysts** are in the same phase as the reactants. **Heterogeneous catalysts** provide a path of lower activation energy by having a surface on which the reactants are adsorbed and react. Catalysts in living systems are called enzymes.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Factors that affect reaction rates (page 637)

The five factors that affect the rate of reactions are (1) the chemical nature of the reactants; (2) the ability of the reactants to come in contact with each other; (3) the concentrations of the reactants; (4) the temperature of the reaction; and (5) the availability of catalysts.

Rate with respect to one reactant of product (page 639)

This is the instantaneous rate of the reaction with respect to one reactant or product. It can be determined by measuring the change in concentration versus time for the tangent to the curve of time versus concentration at the given time.

$$\text{Rate} = \frac{\Delta(\text{conc. of } X)}{\Delta t}$$

The rates are always expressed as a positive value, so if the concentration is decreasing for a reactant, the sign is changed to the positive.

Rate of a reaction (page 642)

The rate of a reaction does not change with what is being monitored. Therefore, for the reaction,

$$aA + bB \longrightarrow cC + dD$$

the rate expression is

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Rate law of a reaction (page 645)

A rate law allows us to calculate the rate of reaction for a given set of reactant concentrations. It also serves as a guide in devising reasonable reaction mechanisms. Exponents for the concentrations in the rate law are always determined experimentally, as described on page 648. Rate constants determined at different temperatures are used in the Arrhenius equation described below:

$$\text{rate} = k\,[A]^n\,[B]^m$$

Determining the order of reactions (page 648)

In the rate law, the order of the reaction is the sum of the exponents for the concentrations of the reactants. The order of the reaction can only be determined by experiment. Data are obtained from experiments conducted under different sets of conditions. For example, the concentration of one reactant may be changed, then the ratios of the rates to the concentrations are compared:

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2{}^n[B]_2{}^m}{k[A]_1{}^n[B]_1{}^m} = \frac{k}{k}\left(\frac{[A]_2}{[A]_1}\right)^n\left(\frac{[B]_2}{[B]_1}\right)^m$$

Integrated first-order rate law (page 654)

For a first-order reaction with known k, this equation is used when we need to calculate the concentration of a reactant at some specified time after the start of the reaction. We could also calculate the time required for the concentration to drop to some specified value. This equation is also used for the carbon-14 dating of organic materials.

$$\ln\frac{[A]_0}{[A]_t} = kt$$

Half-lives of first-order reactions (page 657)

This equation relates the rate constant to the half-life, $t_{1/2}$, for first-order reactions. Use of half-lives can be a convenient alternative to the integrated first-order rate law to determine the concentration of a reactant after it has reacted for a whole number of half-lives. The amount of reactant left after n half-lives is equal to $\left(\frac{1}{2}\right)^n$.

$$\ln 2 = kt_{1/2}$$

Carbon-14 dating (page 660)

Carbon-14 dating is a special example of a half-life of a first-order reaction. The half-life for carbon-14 is 5730 years and the rate constant is $1.21 \times 10^{-4}\ \text{yr}^{-1}$. The age of an object can be found by comparing the ratio of $^{14}C/^{12}C$, r_t, from an object in question to the ratio of $^{14}C/^{12}C$ in a contemporary sample, r_0.

$$\ln\frac{r_0}{r_t} = (1.21 \times 10^{-4}\ \text{yr}^{-1})t$$

Integrated second-order rate law (page 661)

For a second-order reaction of the form, rate $= k[B]^2$, with known k, this equation is used to calculate the concentration of a reactant at some specified time after the start of the reaction, or the time required for the concentration to decrease to some specified value.

$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt$$

Integrated zero-order rate law (page 663)

In a zero-order rate law with the form, rate $= k$, the rate is independent of the concentration of the reactants. The integrated rate law is

$$[A]_t = -kt + [A]_0$$

Arrhenius equation (page 669)

This equation relates the rate constant, k, to the activation energy, E_a, and temperature. Activation energies are determined by measuring rate constants at a variety of temperatures and graphically analyzing the data (see page 671). This equation is also used to determine the shelf life of a wide variety of consumer products.

$$k = A\,e^{-E_a/RT}$$

Arrhenius equation, alternate form (page 672)

The rate constants for a reaction at two different temperatures are related by the alternate form of the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rate laws for elementary processes (page 676)

The exponents in the rate laws are equal to the coefficients of the reactants in the chemical equations for that elementary process.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Factors that Affect Reaction Rate

14.1 Give an example from everyday experience of **(a)** a very fast reaction, **(b)** a moderately fast reaction, and **(c)** a slow reaction.

14.2 Suppose we compared two reactions, one requiring the simultaneous collision of three molecules and the other requiring a collision between two molecules. From the standpoint of statistics, and all other factors being equal, which reaction should be faster? Explain your answer.

14.3 How does an instantaneous rate of reaction differ from an average rate of reaction?

14.4 Explain how the initial instantaneous rate of reaction can be determined from experimental concentration versus time data.

14.5 What is a *homogeneous reaction*? What is a *heterogeneous reaction*? Give examples.

14.6 Why are chemical reactions usually carried out in solution?

14.7 What is the major factor that affects the rate of a heterogeneous reaction?

14.8 How does particle size affect the rate of a heterogeneous reaction? Why?

14.9 The rate of hardening of epoxy glue depends on the amount of hardener that is mixed into the glue. What factor affecting reaction rates does this illustrate?

14.10 A Polaroid™ instant photograph develops faster if it's kept warm than if it is exposed to cold. Why?

14.11 Insects have no way of controlling their body temperatures like mammals do. In cool weather, they become sluggish and move less quickly. How can this be explained using the principles developed in this chapter?

14.12 Persons who have been submerged in very cold water and who are believed to have drowned sometimes can be revived. On the other hand, persons who have been submerged in warmer water for the same length of time have died. Explain this in terms of factors that affect the rates of chemical reactions.

Concentration and Rate; Rate Laws

14.13 What are the units of reaction rate? What is the sign of a reaction rate?

14.14 What are the units of the rate constant for **(a)** a first-order reaction, **(b)** a second-order reaction, and **(c)** a zero-order reaction?

14.15 How does the dependence of reaction rate on concentration differ between a zero-order and a first-order reaction? Between a first-order and second-order reaction?

14.16 Is there any way of using the coefficients in the balanced overall equation for a reaction to predict with certainty what the exponents are in the rate law?

14.17 If the concentration of a reactant is doubled and the reaction rate is unchanged, what must be the order of the reaction with respect to that reactant?

14.18 If the concentration of a reactant is doubled and the reaction rate doubles, what must be the order of the reaction with respect to that reactant?

14.19 If the concentration of a reactant is doubled, by what factor will the rate increase if the reaction is second order with respect to that reactant?

14.20 In an experiment, the concentration of a reactant was tripled. The rate increased by a factor of 27. What is the order of the reaction with respect to that reactant?

14.21 Biological reactions usually involve the interaction of an enzyme with a *substrate*, the substance that actually undergoes the chemical change. In many cases, the rate of reaction depends on the concentration of the enzyme but is independent of the substrate concentration. What is the order of the reaction with respect to the substrate in such instances?

Concentration and Time, Half-Lives

14.22 How is the half-life of a first-order reaction affected by the initial concentration of the reactant?

14.23 How is the half-life of a second-order reaction affected by the initial reactant concentration?

14.24 How is the half-life of a zero-order reaction affected by the initial reactant concentration?

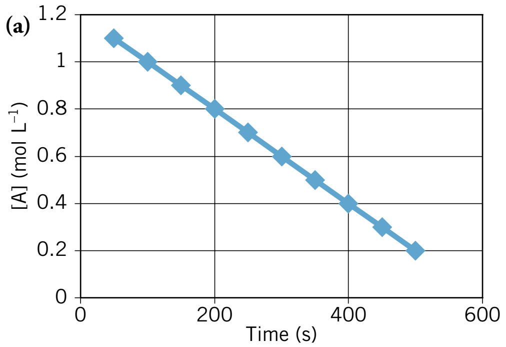
14.25 Derive the equations for $t_{1/2}$ for first-, second-, and zero-order reactions from Equations 14.5, 14.10, and 14.12, respectively.

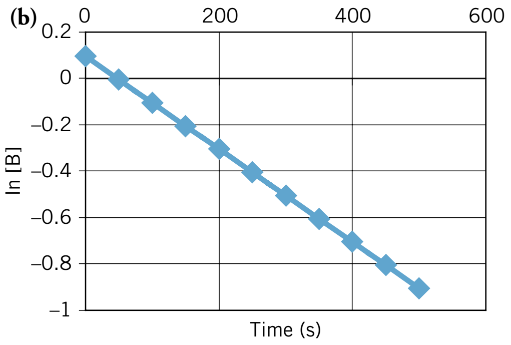
14.26 The integrated rate law for a zero-order reaction is

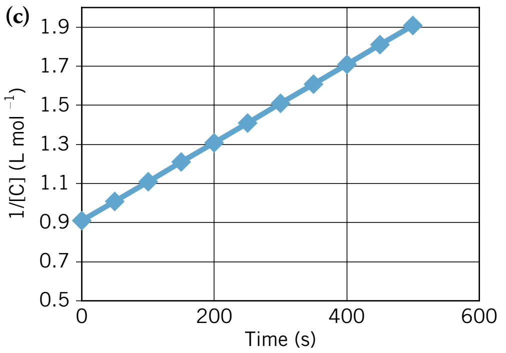
$$[A]_t - [A]_0 = kt$$

Derive an equation for the half-life of a zero-order reaction.

14.27 Which of the following graphs represents the data collected for a first-order reaction? A second-order reaction? A zero-order reaction?







Effect of Temperature on Rate

14.28 What is the basic postulate of collision theory?

14.29 What two factors influence the effectiveness of molecular collisions in producing chemical change?

14.30 In terms of the kinetic theory, why does an increase in temperature increase the reaction rate?

14.31 Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reactions. Also indicate the heat of reaction.

14.32 Draw a potential energy diagram for an exothermic reaction and indicate on the diagram the location of the transition state.

14.33 The decomposition of carbon dioxide,

$$CO_2 \longrightarrow CO + O$$

has an activation energy of approximately 460 kJ/mol. Explain why this large value is consistent with a mechanism that involves the breaking of a C═O bond.

Reaction Mechanisms

14.34 What is the definition of an *elementary process?* How are elementary processes related to the mechanism of a reaction?

14.35 What is a *rate-determining step*?

14.36 In what way is the rate law for a reaction related to the rate-determining step?

14.37 A reaction has the following mechanism:

$$\begin{aligned} 2NO &\longrightarrow N_2O_2 \\ N_2O_2 + H_2 &\longrightarrow N_2O + H_2O \\ N_2O + H_2 &\longrightarrow N_2 + H_2O \end{aligned}$$

What is the net overall change that occurs in this reaction? Identify any intermediates in the reaction.

14.38 If the reaction, $NO_2 + CO \longrightarrow NO + CO_2$, occurs by a one-step collision process, what would be the expected rate law for the reaction? The actual rate law is rate $= k\,[NO_2]^2$. Could the reaction actually occur by a one-step collision between NO_2 and CO? Explain.

14.39 The oxidation of NO to NO_2, one of the reactions in the production of smog, appears to involve carbon monoxide. A possible mechanism is

$$\begin{aligned} CO + \cdot OH &\longrightarrow CO_2 + H\cdot \\ H\cdot + O_2 &\longrightarrow HOO\cdot \\ HOO\cdot + NO &\longrightarrow \cdot OH + NO_2 \end{aligned}$$

(The formulas with dots represent extremely reactive species with unpaired electrons and are called *free radicals.*) Write the net chemical equation for the reaction.

14.40 Show that the following two mechanisms give the same net overall reaction.

Mechanism 1

$$\begin{aligned} OCl^- + H_2O &\longrightarrow HOCl + OH^- \\ HOCl + I^- &\longrightarrow HOI + Cl^- \\ HOI + OH^- &\longrightarrow H_2O + OI^- \end{aligned}$$

Mechanism 2

$$\begin{aligned} OCl^- + H_2O &\longrightarrow HOCl + OH^- \\ I^- + HOCl &\longrightarrow ICl + OH^- \\ ICl + 2OH^- &\longrightarrow OI^- + Cl^- + H_2O \end{aligned}$$

14.41 The experimental rate law for the reaction, $NO_2 + CO \longrightarrow CO_2 + NO$, is rate $= k\,[NO_2]^2$. If the mechanism is

$$\begin{aligned} 2NO_2 &\longrightarrow NO_3 + NO \qquad \text{(slow)} \\ NO_3 + CO &\longrightarrow NO_2 + CO_2 \qquad \text{(fast)} \end{aligned}$$

show that the predicted rate law is the same as the experimental rate law.

Catalysts

14.42 How does a catalyst increase the rate of a chemical reaction?

14.43 What is a *homogeneous catalyst*? How does it function, in general terms?

14.44 What is the difference in meaning between the terms *adsorption* and *absorption*? (If necessary, use a dictionary.) Which one applies to heterogeneous catalysts?

14.45 What does the catalytic converter do in the exhaust system of an automobile? Why should leaded gasoline not be used in cars equipped with catalytic converters?

Review Problems

Measuring Rates of Reaction

14.46 The following data were collected at a certain temperature for the decomposition of sulfuryl chloride, SO_2Cl_2, a chemical used in a variety of organic syntheses.

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

Time (min)	$[SO_2Cl_2]$ (mol L^{-1})
0	0.1000
1.00×10^2	0.0876
2.00×10^2	0.0768
3.00×10^2	0.0673
4.00×10^2	0.0590
5.00×10^2	0.0517
6.00×10^2	0.0453
7.00×10^2	0.0397
8.00×10^2	0.0348
9.00×10^2	0.0305
1.000×10^3	0.0267
1.100×10^3	0.0234

Make a graph of concentration versus time and determine the instantaneous rate of formation of SO_2 using the tangent to the curve at $t = 200$ minutes and $t = 600$ minutes.

14.47 The following data were collected for the decomposition of acetaldehyde, CH_3CHO (used in the manufacture of a variety of chemicals including perfumes, dyes, and plastics), into methane and carbon monoxide. The data were collected at 535 °C.

$$CH_3CHO \longrightarrow CH_4 + CO$$

$[CH_3CHO]$ (mol L^{-1})	Time (s)
0.200	0
0.153	0.20×10^2
0.124	0.40×10^2
0.104	0.60×10^2
0.090	0.80×10^2
0.079	1.00×10^2
0.070	1.20×10^2
0.063	1.40×10^2
0.058	1.60×10^2
0.053	1.80×10^2
0 049	2.00×10^2

Make a graph of concentration versus time and determine, using the tangent to the curve, the instantaneous rate of reaction of CH_3CHO after 60 seconds and after 120 seconds.

14.48 In the reaction, $3H_2 + N_2 \longrightarrow 2NH_3$, how does the rate of disappearance of hydrogen compare to the rate of disappearance of nitrogen? How does the rate of appearance of NH_3 compare to the rate of disappearance of nitrogen?

OH **14.49** For the reaction, $2A + B \longrightarrow 3C$, it was found that the rate of disappearance of B was 0.30 mol L^{-1} s^{-1}. What were the rate of disappearance of A and the rate of appearance of C?

14.50 In the combustion of hexane (a low-boiling component of gasoline),

$$2C_6H_{14}(g) + 19O_2(g) \longrightarrow 12CO_2(g) + 14H_2O(g)$$

it was found that the rate of reaction of C_6H_{14} was 1.20 mol L^{-1} s^{-1}.

(a) What was the rate of reaction of O_2?

(b) What was the rate of formation of CO_2?

(c) What was the rate of formation of H_2O?

14.51 At a certain moment in the reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

N_2O_5 is decomposing at a rate of 2.5×10^{-6} mol L^{-1} s^{-1}. What are the rates of formation of NO_2 and O_2?

14.52 Consider the reaction,

$$CH_3Cl(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + 3HCl(g).$$

(a) Express the rate of the reaction with respect to each of the reactants and products.

(b) If the instantaneous rate of the reaction with respect to HCl is 0.029 $M\ s^{-1}$, what is the instantaneous rate of the reaction?

14.53 The decomposition of phosphine, a very toxic gas, forms phosphorus and hydrogen in the following reaction:

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

(a) Express the rate of the reaction with respect to each of the reactants and products.

(b) If the instantaneous rate of the reaction with respect to PH_3 is 0.34 $M\ s^{-1}$, what is the instantaneous rate of the reaction?

Rate Laws for Reactions

14.54 Estimate the rate of the reaction,

$$H_2SeO_3 + 6I^- + 4H^+ \longrightarrow Se + 2I_3^- + 3H_2O$$

given that the rate law for the reaction at 0 °C is

$$\text{rate} = (5.0 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1})[H_2SeO_3]\,[I^-]^3\,[H^+]^2$$

The reactant concentrations are $[H_2SeO_3] = 2.0 \times 10^{-2}\ M$, $[I^-] = 2.0 \times 10^{-3}\ M$, and $[H^+] = 1.0 \times 10^{-3}\ M$.

14.55 Estimate the rate of the reaction,

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

given the rate law for the reaction is

$$\text{rate} = (1.3 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1})\,[OH^-][H^+]$$

for neutral water, where $[H^+] = 1.0 \times 10^{-7}\ M$ and $[OH^-] = 1.0 \times 10^{-7}\ M$.

OH **14.56** The oxidation of NO (released in small amounts in the exhaust of automobiles) produces the brownish-red gas NO_2, which is a component of urban air pollution.

$$2NO + O_2 \longrightarrow 2NO_2$$

The rate law for the reaction is rate $= k\,[NO]^2\,[O_2]$. At 25 °C, $k = 7.1 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. What would be the rate of the reaction if $[NO] = 0.0010 \text{ mol L}^{-1}$ and $[O_2] = 0.034 \text{ mol L}^{-1}$?

14.57 The rate law for the decomposition of N_2O_5 is

$$\text{rate} = k[N_2O_5]$$

If $k = 1.0 \times 10^{-5} \text{ s}^{-1}$, what is the reaction rate when the N_2O_5 concentration is $0.0010 \text{ mol L}^{-1}$?

14.58 The rate law for a certain enzymatic reaction is zero order with respect to the substrate. The rate constant for the reaction is $6.4 \times 10^2\ M \text{ s}^{-1}$. If the initial concentration of the substrate is 0.275 mol L^{-1}, what is the initial rate of the reaction?

14.59 Radon-220 is radioactive, and decays into polonium-216. This is a first-order process, just like the radioactive decay of carbon-14, and it has a rate constant of 0.0125 s^{-1}. When the concentration of radon-220 is $1.0 \times 10^{-9} \text{ mol L}^{-1}$, what is the rate of the reaction?

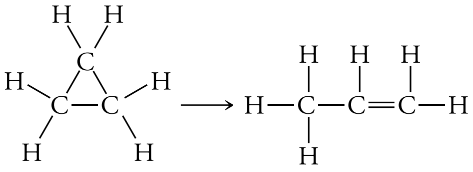
14.60 The following data were collected for the reaction

$$M + N \longrightarrow P + Q$$

Initial Concentrations (mol L^{-1})		Initial Rate of Reaction
[*M*]	[*N*]	(mol L^{-1} s^{-1})
0.010	0.010	2.5×10^{-3}
0.020	0.010	5.0×10^{-3}
0.020	0.030	4.5×10^{-2}

What is the rate law for the reaction? What is the value of the rate constant (with correct units)?

14.61 Cyclopropane, C_3H_6, is a gas used as a general anesthetic. It undergoes a slow molecular rearrangement to propylene.



cyclopropane propylene

At a certain temperature, the following data were obtained relating concentration and rate:

Initial Concentration of Cyclopropane (mol L^{-1})	Rate of Formation of Propylene (mol L^{-1} s^{-1})
0.050	2.95×10^{-5}
0.100	5.90×10^{-5}
0.150	8.85×10^{-5}

What is the rate law for the reaction? What is the value of the rate constant, with correct units?

14.62 The reaction of iodide ion with hypochlorite ion, OCl^- (the active ingredient in a "chlorine bleach" such as Clorox), follows the equation $OCl^- + I^- \longrightarrow OI^- + Cl^-$. It is a rapid reaction that gives the following rate data:

Initial Concentrations (mol L^{-1})		Rate of Formation of Cl$^-$
[OCl$^-$]	[I$^-$]	(mol L^{-1} s^{-1})
1.6×10^{-3}	1.6×10^{-3}	1.75×10^4
7.6×10^{-3}	1.6×10^{-3}	8.31×10^4
1.6×10^{-3}	9.6×10^{-3}	1.05×10^5

What is the rate law for the reaction? Determine the value of the rate constant with its correct units.

14.63 The formation of small amounts of nitric oxide, NO, in automobile engines is the first step in the formation of smog. As noted in Problem 14.56, nitric oxide is readily oxidized to nitrogen dioxide by the reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

The following data were collected in a study of the rate of this reaction:

Initial Concentrations (mol L^{-1})		Rate of Formation of NO$_2$
[O$_2$]	[NO]	(mol L^{-1} s^{-1})
0.0010	0.0010	7.10
0.0037	0.0010	26.3
0.0037	0.0062	1011

What is the rate law for the reaction? What is the rate constant with its correct units?

OH **14.64** At a certain temperature, the following data were collected for the reaction, $2ICl + H_2 \rightarrow I_2 + 2HCl$:

Initial Concentrations ($mol\ L^{-1}$)		Initial Rate of Formation of I_2
[ICl]	**[H_2]**	**($mol\ L^{-1}\ s^{-1}$)**
0.12	0.12	0.0015
0.78	0.12	0.0098
0.12	0.089	0.0011

Determine the rate law and the rate constant (with correct units) for the reaction.

14.65 The following data were obtained for the reaction of $(CH_3)_3CBr$ with hydroxide ion at 55 °C.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

Initial Concentrations ($mol\ L^{-1}$)		Initial Rate of Formation of $(CH_3)_3COH$
[$(CH_3)_3CBr$]	**[OH^-]**	**($mol\ L^{-1}\ s^{-1}$)**
0.19	0.10	1.0×10^{-3}
0.46	0.10	2.4×10^{-3}
0.73	0.10	3.8×10^{-3}
0.19	0.25	1.0×10^{-3}
0.19	0.37	1.0×10^{-3}

What is the rate law for the reaction? What is the value of the rate constant (with correct units) at this temperature?

Concentration and Time

14.66 Data for the decomposition of SO_2Cl_2 according to the equation $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$, were given in Problem 14.46. Show graphically that these data fit a first-order rate law. Graphically determine the rate constant for the reaction.

14.67 For the data in Problem 14.47, decide graphically whether the reaction is first or second order. Graphically determine the rate constant for the reaction described in that problem.

OH ILW **14.68** The decomposition of SO_2Cl_2 described in Problem 14.46 has a first-order rate constant, $k = 2.2 \times 10^{-5}$ s^{-1} at 320 °C. If the initial SO_2Cl_2 concentration in a container is 0.0040 *M*, what will its concentration be **(a)** after 1.00 hour and **(b)** after 1.00 day?

14.69 The decomposition of acetaldehyde, CH_3CHO, was described in Problem 14.47, and the order of the reaction and the rate constant for the reaction at 530 °C were determined in Problem 14.67. If the initial concentration of acetaldehyde is 0.300 *M*, what will the concentration be **(a)** after 30 minutes, **(b)** after 180 minutes?

14.70 If it takes 75.0 min for the concentration of a reactant to drop to 25.0% of its initial value in a first-order reaction, what is the rate constant for the reaction in the units min^{-1}?

14.71 It takes 15.4 minutes for the concentration of a reactant to drop to 5.0% of its initial value in a second-order reaction. What is the rate constant for the reaction in the units $L\ mol^{-1}\ min^{-1}$?

14.72 The concentration of a drug in the body is often expressed in units of milligrams per kilogram of body weight. The initial dose of a drug in an animal was 25.0 mg/kg body weight. After 2.00 hours, this concentration had dropped to 15.0 mg/kg body weight. If the drug is eliminated metabolically by a first-order process, what is the rate constant for the process in units of min^{-1}?

14.73 Phosphine, PH_3, decomposes into phosphorus, P_4, and hydrogen at 680 °C, as described in Problem 14.53. If the initial concentration of phosphine is $1.1 \times 10^{-6}\ g\ L^{-1}$, and after 180 s the concentration has dropped to 0.30×10^{-6} $g\ L^{-1}$, what is the rate constant for this process in s^{-1}?

14.74 Hydrogen iodide decomposes according to the equation, $2HI(g) \longrightarrow H_2(g) + I_2(g)$. The reaction is second order and has a rate constant equal to $1.6 \times 10^{-3}\ L\ mol^{-1}\ s^{-1}$ at 750 °C. If the initial concentration of HI in a container is 3.4×10^{-2} *M*, how many minutes will it take for the concentration to be reduced to 8.0×10^{-4} *M*?

14.75 The reaction of $NOBr(g)$ to form $NO(g)$ and $Br_2(g)$ is second order:

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$$

The rate constant is $0.556\ L\ mol^{-1}\ s^{-1}$ at some temperature. If the initial concentration of NOBr in the container is 0.25 *M*, how long will it take for the concentration to decrease to 0.025 *M*?

14.76 Using the information determined in Problem 14.72, calculate what the initial dose of the drug must be in order for the drug concentration 3.00 hours afterward to be 5.0 mg/kg body weight.

14.77 The second-order rate constant for the decomposition of HI at 750 °C was given in Problem 14.74. At 2.5×10^3 minutes after a particular experiment had begun, the HI concentration was equal to $4.5 \times 10^{-4}\ mol\ L^{-1}$. What was the initial molar concentration of HI in the reaction vessel?

Half-Lives

14.78 The half-life of a certain first-order reaction is 15 minutes. What fraction of the original reactant concentration will remain after 2.0 hours?

14.79 Strontium-90 has a half-life of 28 years. How long will it take for all of the strontium-90 presently on earth to be reduced to 1/32nd of its present amount?

14.80 Using the graph from Problem 14.46, determine the time required for the SO_2Cl_2 concentration to drop from $0.100\ mol\ L^{-1}$ to $0.050\ mol\ L^{-1}$. How long does it take for the concentration to drop from $0.050\ mol\ L^{-1}$ to $0.025\ mol\ L^{-1}$? What is the order of this reaction? (*Hint:* How is the half-life related to concentration?)

14.81 Using the graph from Problem 14.47, determine how long it takes for the CH_3CHO concentration to decrease from 0.200 mol L^{-1} to 0.100 mol L^{-1}. How long does it take the concentration to drop from 0.100 mol L^{-1} to 0.050 mol L^{-1}? What is the order of this reaction? (*Hint:* How is the half-life related to concentration?)

14.82 Hydrogen peroxide, which decomposes in a first-order reaction, has a half-life of 10 hours in air. How long will it take for hydrogen peroxide to decompose to 10% of its original concentration?

14.83 SO_2Cl_2 decomposes in a first-order process with a half life of 4.88×10^3 s. If the original concentration of SO_2Cl_2 is 0.012 M, how many seconds will it take for the SO_2Cl_2 to reach 0.0020 M?

Radiological Dating

14.84 A 500 mg sample of rock was found to have 2.45×10^{-6} mol of potassium-40 ($t_{1/2} = 1.3 \times 10^9$ yr) and 2.45×10^{-6} mol of argon-40. How old was the rock? (*Hint:* What assumption is made about the origin of the argon-40?)

ILW **14.85** A tree killed by being buried under volcanic ash was found to have a ratio of carbon-14 atoms to carbon-12 atoms of 4.8×10^{-14}. How long ago did the eruption occur?

14.86 A wooden door lintel from an excavated site in Mexico would be expected to have what ratio of carbon-14 to carbon-12 atoms if the lintel is 9.0×10^3 years old?

14.87 If a rock sample was found to contain 1.16×10^{-7} mol of argon-40, how much potassium-40 ($t_{1/2} = 1.3 \times 10^9$ yr) would also have to be present for the rock to be 1.3×10^9 years old? See assumption in Problem 14.84.

Calculations Involving the Activation Energy

14.88 The following data were collected for a reaction:

Rate Constant (L mol^{-1} s^{-1})	Temperature (°C)
2.88×10^{-4}	3.20×10^2
4.87×10^{-4}	3.40×10^2
7.96×10^{-4}	3.60×10^2
1.26×10^{-3}	3.80×10^2
1.94×10^{-3}	4.00×10^2

Determine the activation energy for the reaction in kJ/mol both graphically and by calculation using Equation 14.15. For the calculation of E_a, use the first and last sets of data in the table.

14.89 Rate constants were measured at various temperatures for the reaction, $HI(g) + CH_3I(g) \longrightarrow CH_4(g) + I_2(g)$. The following data were obtained:

Rate Constant (L mol^{-1} s^{-1})	Temperature (°C)
1.91×10^{-2}	2.05×10^2
2.74×10^{-2}	2.10×10^2
3.90×10^{-2}	2.15×10^2
5.51×10^{-2}	2.20×10^2
7.73×10^{-2}	2.25×10^2
1.08×10^{-1}	2.30×10^2

Determine the activation energy in kJ/mol both graphically and by calculation using Equation 14.15. For the calculation of E_a, use the first and last sets of data in the table.

ILW OH **14.90** The decomposition of NOCl, $2NOCl \longrightarrow 2NO + Cl_2$, has $k = 9.3 \times 10^{-5}$ L mol^{-1} s^{-1} at 100 °C and $k = 1.0 \times 10^{-3}$ L mol^{-1} s^{-1} at 130 °C. What is E_a for this reaction in kJ mol^{-1}? Use the data at 373 K to calculate the frequency factor, A. What is the rate constant at 473 K?

14.91 The conversion of cyclopropane, an anesthetic, to propylene (see Problem 14.61) has a rate constant $k = 1.3 \times 10^{-6}$ s^{-1} at 673 K and $k = 1.1 \times 10^{-5}$ s^{-1} at 703 K.

(a) What is the activation energy in kJ/mol?

(b) Use the data given at 703 K to calculate the frequency factor, A, for this reaction?

(c) What is the rate constant for the reaction at 350 °C?

14.92 The decomposition of N_2O_5 has an activation energy of 103 kJ/mol and a frequency factor of 4.3×10^{13} s^{-1}. What is the rate constant for this decomposition at **(a)** 25 °C and **(b)** 373 K?

14.93 At 35 °C, the rate constant for the reaction

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

is $k = 6.2 \times 10^{-5}$ s^{-1}. The activation energy for the reaction is 108 kJ mol^{-1}. What is the rate constant for the reaction at 45 °C?

Mechanisms of Reactions

14.94 Consider the general reaction

$$AB + C \longrightarrow AC + B$$

If this reaction occurs in one step, what would be the expected rate law for the reaction?

14.95 Nitrogen dioxide reacts with carbon monoxide to produce nitrogen monoxide and carbon dioxide in the reaction, $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$. The first step in the reaction is proposed to be two NO_2 molecules colliding to form NO_3 and NO. The NO_3 intermediate then reacts with CO to form CO_2. What is the rate law for this proposed mechanism?

14.96 The oxidation of nitrogen monoxide with oxygen to nitrogen dioxide has a possible mechanism of

$$2NO(g) \rightleftharpoons N_2O_2(g) \qquad \text{(fast)}$$
$$N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \text{(slow)}$$

What are the intermediates in the proposed mechanism? What is the balanced equation for the overall reaction? What is the rate law for the reaction?

14.97 The reaction of chloroform and chlorine forms carbon tetrachloride and hydrogen chloride in the following proposed mechanism:

$$Cl_2(g) \rightleftharpoons 2Cl(g) \qquad \text{(fast)}$$

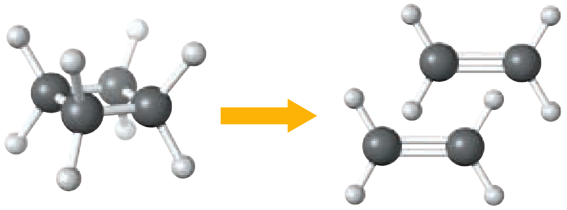
$$Cl(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_3(g) \qquad \text{(slow)}$$

$$CCl_3(g) + Cl(g) \longrightarrow CCl_4(g) \qquad \text{(fast)}$$

What are the intermediates in the proposed mechanism? What is the balanced equation for the overall reaction? What is the rate law for the reaction?

| Additional Exercises

14.98 The following data were collected for the reaction of cyclobutane, $C_4H_8(g)$, to form ethylene, $C_2H_4(g)$.



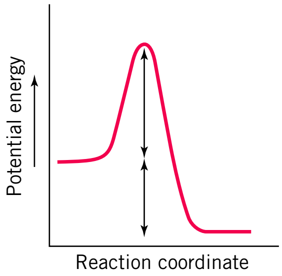
$$C_4H_8(g) \longrightarrow 2C_2H_4(g)$$

Time (min)	$[C_4H_8]$ (mol L^{-1})
0	0.00912
2.00×10^3	0.00720
4.00×10^3	0.00565
6.00×10^3	0.00447
8.00×10^3	0.00353
1.00×10^4	0.00278

Make a graph of concentration versus time for the *formation* of C_2H_4 and the decomposition of C_4H_8 on the same graph. What are the rates of formation of C_2H_4 at $t = 1.00 \times 10^3$ s and $t = 9.00 \times 10^3$ s, and the rates of decomposition of C_4H_8 at $t = 1.00 \times 10^3$ s and $t = 9.00 \times 10^3$ s? What can be said about the relationship between the values of the rates of formation and decomposition?

14.99 The age of wine can be determined by measuring the trace amount of radioactive tritium, ^3H, present in a sample. Tritium is formed from hydrogen in water vapor in the upper atmosphere by cosmic bombardment, so all naturally occurring water contains a small amount of this isotope. Once the water is in a bottle of wine, however, the formation of additional tritium from the water is negligible, so the tritium initially present gradually diminishes by a first-order radioactive decay with a half-life of 12.5 years. If a bottle of wine is found to have a tritium concentration that is 0.100 that of freshly bottled wine (i.e., $[^3H]_t = 0.100\,[^3H]_0$), what is the age of the wine?

14.100 On the following graph, label the products, reactant, $\Delta H_{\text{reaction}}$, the energy of activation (E_a) and the transition state. Is the reaction exothermic or endothermic? On the graph, draw a path for a catalyzed reaction.



OH **14.101** Carbon-14 dating can be used to estimate the age of formerly living materials because the uptake of carbon-14 from carbon dioxide in the atmosphere stops once the organism dies. If tissue samples from a mummy contain about 81.0% of the carbon-14 expected in living tissue, how old is the mummy? The half-life for decay of carbon-14 is 5730 years.

***14.102** What percentage of cesium chloride made from cesium-137 ($t_{1/2} = 30$ yr) remains after 150 years? What *chemical* product forms?

14.103 For the following reactions, predict how the rate of the reaction will change as the concentration of the reactants triple.

(a) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2 \quad \text{rate} = k[SO_2Cl_2]$

(b) $2HI \longrightarrow H_2 + I_2 \quad \text{rate} = k[HI]^2$

(c) $ClOO \longrightarrow Cl + O_2 \quad \text{rate} = k$

(d) $NH_4 + (aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$
$\text{rate} = k[NH_4^+][NO_2^-]$

(e) $2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$
$\text{rate} = k[H_2][NO]^2$

***14.104** One of the reactions that occurs in polluted air in urban areas is $2NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g)$. It is believed that a species with the formula NO_3 is involved in the mechanism, and the observed rate law for the overall reaction is rate $= k[NO_2][O_3]$. Propose a mechanism for this reaction that includes the species NO_3 and is consistent with the observed rate law.

OH ***14.105** Suppose a reaction occurs with the following mechanism:

$$(1)\ 2A \rightleftharpoons A_2 \qquad \text{(fast)}$$

$$(2)\ A_2 + E \longrightarrow B + C \qquad \text{(slow)}$$

in which the first step is a very rapid reversible reaction that can be considered to be essentially an equilibrium (forward and reverse reactions occurring at the same rate) and the second is a slow step.

(a) Write the rate law for the forward reaction in step (1).

(b) Write the rate law for the reverse reaction in step (1).

(c) Write the rate law for the rate-determining step.

(d) What is the chemical equation for the net reaction that occurs in this chemical change?

(e) Use the results of parts (a) and (b) to rewrite the rate law of the rate-determining step in terms of the concentrations of the reactants in the overall balanced chemical equation for the reaction.

OH **14.106** The decomposition of urea, $(NH_2)_2CO$, in 0.10 *M* HCl follows the equation

$$(NH_2)_2CO(aq) + 2H^+(aq) + H_2O \longrightarrow 2NH_4^+(aq) + CO_2(g)$$

At 65 °C, $k = 5.84 \times 10^{-6}\ \text{min}^{-1}$, and at 75 °C, $k = 2.25 \times 10^{-5}\ \text{min}^{-1}$. If this reaction is run at 85 °C starting with a urea concentration of 0.0020 *M*, how many minutes will it take for the urea concentration to drop to 0.0012 *M*?

14.107 Show that for a reaction that obeys the general rate law,

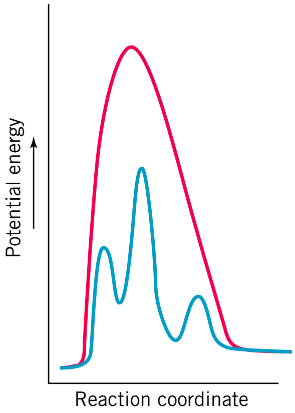
$$\text{rate} = k\,[A]^n$$

a graph of log(rate) versus log $[A]$ should yield a straight line with a slope equal to the order of the reaction. For the reaction in Problem 14.46, measure the rate of the reaction at $t = 150, 300, 450$, and 600 s. Then graph log(rate) versus $\log[SO_2Cl_2]$ and determine the order of the reaction with respect to SO_2Cl_2.

OH ***14.108** The rates of many reactions approximately double for each 10 °C rise in temperature. Assuming a starting temperature of 25 °C, what would the activation energy be, in kJ mol^{-1}, if the rate of a reaction were to be twice as large at 35 °C?

14.109 If the rate constant for a first-order reaction is doubled by heating the reaction what happens to the rate of the reaction if the concentration is kept the same?

***14.110** For the following potential energy diagram, which path represents a catalyzed reaction? How many steps would be proposed in the mechanism for the catalyzed reaction, and which step would be rate-determining?



***14.111** The development of a photographic image on film is a process controlled by the kinetics of the reduction of silver halide by a developer. The time required for development at a particular temperature is inversely proportional to the rate constant for the process. Below are published data on development times for Kodak's Tri-X film using Kodak D-76 developer. From these data, estimate the activation energy (in units of kJ mol^{-1}) for the development process. Also estimate the development time at 15 °C.

Temperature (°C)	Development Time (minutes)
18	10
20	9
21	8
22	7
24	6

14.112 The rate at which crickets chirp depends on the ambient temperature, because crickets are cold-blooded insects whose body temperature follows the temperature of their environment. It has been found that the Celsius temperature can be estimated by counting the number of chirps in 8 seconds and then adding 4. In other words, t_C = (number of chirps in 8 seconds) + 4.

(a) Calculate the number of chirps in 8 seconds for temperatures of 20, 25, 30, and 35 °C.

(b) The number of chirps per unit of time is directly proportional to the rate constant for a biochemical reaction involved in the cricket's chirp. On the basis of this assumption, make a graph of ln(chirps in 8 s) versus $(1/T)$. Calculate the activation energy for the biochemical reaction involved.

(c) How many chirps would a cricket make in 8 seconds at a temperature of 40 °C?

***14.113** The cooking of an egg involves the denaturation of a protein called albumen. The time required to achieve a particular degree of denaturation is inversely proportional to the rate constant for the process. This reaction has a high activation energy, $E_a = 418\ \text{kJ mol}^{-1}$. Calculate how long it would take to cook a traditional three-minute egg on top of Mt. McKinley in Alaska on a day when the atmospheric pressure there is 355 torr.

***14.114** The following question is based on *Chemistry Outside the Classroom 14.1.* The reaction of hydrogen and bromine appears to follow the mechanism shown,

$$Br_2 \xrightarrow{h\nu} 2Br\cdot$$

$$Br\cdot + H_2 \longrightarrow HBr + H\cdot$$

$$H\cdot + Br_2 \longrightarrow HBr + Br\cdot$$

$$2Br\cdot \longrightarrow Br_2$$

(a) Identify the initiation step in the mechanism.

(b) Identify any propagation steps.

(c) Identify the termination step.

The mechanism also contains the reaction

$$H\cdot + HBr \longrightarrow H_2 + Br\cdot$$

How does this reaction affect the rate of formation of HBr?

14.115 Radioactive samples are considered to become nonhazardous after 10 half-lives. If the half-life is less than 88 days, the radioactive sample can be stored through a decay-in-storage program in which the material is kept in a lead-lined cabinet for at least 10 half-lives. What percent of the initial material will remain after 10 half-lives?

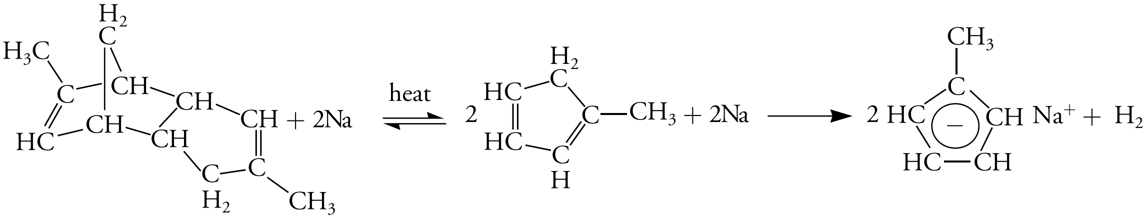
Multi-Concept Problems

***14.116** The catalyzed decomposition of ethanol at 327 °C has a rate constant of 4.00×10^{-5} mol L^{-1} s^{-1}. The plot of concentration of ethanol versus time gives a straight line. The balanced equation for this reaction is

$$C_2H_5OH(g) \longrightarrow C_2H_4(g) + H_2(g)$$

If the initial concentration of ethanol is 0.020 mol L^{-1}, how long will it take for the pressure to reach 1.4 atm at 327 °C?

***14.117** On December 19, 2007, the T2 Laboratories, Inc., reactor exploded in a runaway reaction. The reaction of methyl cyclopentadienyl dimer and sodium produces sodium methyl cyclopentadiene and hydrogen:



The reactor has to be cooled when its temperature reaches 182 °C. On the day of the explosion, the cooling system malfunctioned and the reactor reached 199 °C, at which point a second, more exothermic reaction began to occur. The typical energy of activation for an organic reaction is about 50 kJ/mol. The heat of this reaction is 40 kJ mol^{-1}, and the heat capacity for an industrial scale reaction (i.e., 10,000 mol) can be 7.5×10^6 J $°C^{-1}$. If the rate constant for a typical reaction is 1×10^{-5} s^{-1} at 25 °C, what will be the rate constant, if all the heat is supplied to the reaction all at once, without any external cooling? If the reaction were started at 182 °C, would the reaction reach 199 °C if all the heat were released at once?

Exercises in Critical Thinking

14.118 Provide three examples of ordinary occurrences that mimic a reaction mechanism and have a rate-limiting step.

14.119 Can a reaction have a negative activation energy? Explain your response.

14.120 Assume you have a three-step mechanism. Would the potential energy diagram have three peaks? If so, how would you distinguish the rate-limiting step?

14.121 What range of ages can ^{14}C dating reliably determine?

14.122 Why are initial reaction rates used to determine rate laws?

14.123 If a reaction is reversible (i.e., the products can react to re-form the reactants), what would the rate law look like?

14.124 The ozone layer protects us from high-energy radiation. The description of how the ozone layer works is a kinetics problem concerning the formation and destruction of ozone to produce a steady state. How can we write this mathematically, assuming that the processes are elementary reactions?

14.125 How would you measure the rate of an extremely fast reaction?

14.126 For a reaction done on the ton scale, would a heterogeneous catalyst or a homogeneous catalyst be more effective to use?

14.127 Can we use molality instead of molarity in constructing rate laws? Can mole fractions be used?

15 Chemical Equilibrium

Chapter Outline

15.1 | Dynamic Equilibrium in Chemical Systems

15.2 | Equilibrium Laws

15.3 | Equilibrium Laws Based on Pressures or Concentrations

15.4 | Equilibrium Laws for Heterogeneous Reactions

15.5 | Position of Equilibrium and the Equilibrium Constant

15.6 | Equilibrium and Le Châtelier's Principle

15.7 | Calculating Equilibrium Constants

15.8 | Using Equilibrium Constants to Calculate Concentrations

It is an amazing fact that feeding the earth's enormous (and growing) population relies on a simple chemical equilibrium involving the reaction of nitrogen with hydrogen to form ammonia. This equilibrium, which is one of those discussed in this chapter, is used to manufacture more than 100 million tons of ammonia annually, with most of it going to agricultural uses as a fertilizer. In the pages ahead we will take a close look at chemical equilibria and examine the factors that affect the relative amounts of reactants and products present when a dynamic chemical equilibrium is achieved. Inga Spence/Alamy

This Chapter in Context

In Chapter 14 you learned that most chemical reactions slow down as the reactants are consumed and the products form. The focus there was learning about the factors that affect how *fast* the reactant and product concentrations change. In this and the following four chapters we will turn our attention to the ultimate fate of chemical systems, *dynamic chemical equilibrium*—the situation that exists when the concentrations cease to change.

You have already encountered the concept of a dynamic equilibrium several times in this book. Recall that such an equilibrium is established when two opposing processes occur at equal rates. In a liquid–vapor equilibrium, for example, the processes are evaporation and condensation. In a chemical equilibrium, such as the ionization of a weak acid, they are the forward and reverse reactions represented by the chemical equation. Understanding the factors that affect equilibrium systems is important not only in chemistry but in other sciences as well. They apply to biology because living cells must control the concentrations of substances within them in order to survive. And they are fundamental in understanding chemical reactions that affect many current environmental problems, including global warming, acid rain, and stratospheric ozone depletion.

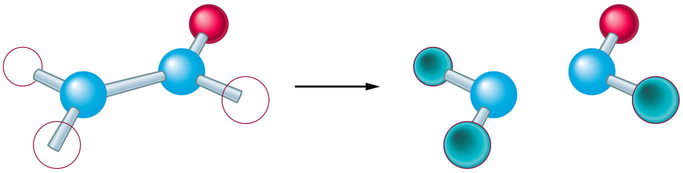
15.1 | Dynamic Equilibrium in Chemical Systems

We begin our discussion of equilibrium by examining principles that apply to chemical systems in general. In Chapters 16 through 18 we will focus on equilibria in aqueous solutions. Then in Chapter 19 we will tie together the concept of chemical equilibrium with the energetics of chemical change.

A Molecular Interpretation of Equilibrium

Let's review the process by which a system reaches equilibrium. For this purpose, we'll examine the reaction for the decomposition of gaseous N_2O_4 into NO_2.

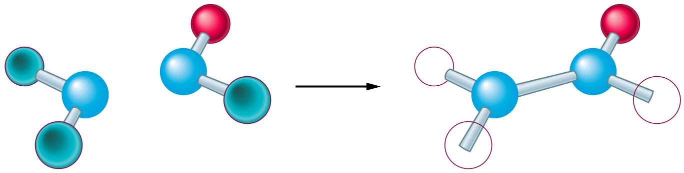
$$N_2O_4(g) \longrightarrow 2NO_2(g) \qquad (15.1)$$



If this reaction were irreversible, over time the concentration of N_2O_4 would continue to drop until it reached zero and all of the N_2O_4 had reacted. However, if we look at what actually happens in the reaction (Figure 15.1), we see that the N_2O_4 concentration decreases until it reaches some final, steady nonzero value. Meanwhile, the NO_2 concentration rises until it also reaches a final steady value.

The explanation for these observations is that the reaction above is actually able to proceed in both directions. As NO_2 is formed and starts to accumulate in the reaction mixture, collisions between NO_2 molecules are able to produce N_2O_4 molecules, so the following reaction begins to occur.

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \textbf{(15.2)}$$



As the NO_2 concentration rises because of Equation 15.1, the rate of the reaction in Equation 15.2 increases. Because N_2O_4 is being remade by Equation 15.2, the drop in N_2O_4 concentration starts to slow down. As you see in Figure 15.1, eventually a state is reached in which the concentrations cease to change. At this point the rate of the forward reaction (Equation 15.1) is equal to the rate of the reverse reaction (Equation 15.2); N_2O_4 is being formed as fast as it's decomposing, and we've reached *dynamic equilibrium*. As you learned in Section 5.3, when we write the equation to describe the equilibrium, we use double arrows ($\rightleftharpoons$).

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \textbf{(15.3)}$$

Most chemical systems eventually reach a state of dynamic equilibrium, given enough time. Sometimes, though, this equilibrium is extremely difficult (or even impossible) to detect, because in some reactions the amounts of either the reactants or products present at equilibrium are virtually zero. For instance, in water vapor at room temperature there are no detectable amounts of either H_2 or O_2 from the equilibrium

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

Water molecules are so stable that we can't detect whether any of them decompose. Even in cases such as this, however, it is often *convenient* to assume that an equilibrium does exist.

■ For the equilibrium A $\rightleftharpoons$ B, the reaction read from left to right is the ***forward reaction***; the reaction read from right to left is the ***reverse reaction***.

A $\longrightarrow$ B (forward reaction)
A $\longleftarrow$ B (reverse reaction)

Remember that even after equilibrium has been reached, both the forward and reverse reactions continue to occur.

The Meaning of *Reactants* and *Products* in a Chemical Equilibrium

For the forward reaction in the equilibrium described by Equation 15.3, N_2O_4 is the reactant and NO_2 is the product. But the reverse reaction is also occurring, where NO_2 is the reactant and N_2O_4 is the product. When the system is at equilibrium, the usual definitions of reactant and product don't make a lot of sense. *In these situations, when we use the term* **reactants**, *we simply mean those substances written to the left of the double arrows. Similarly, we use the term* **products** *to mean the substances to the right of the double arrows.*

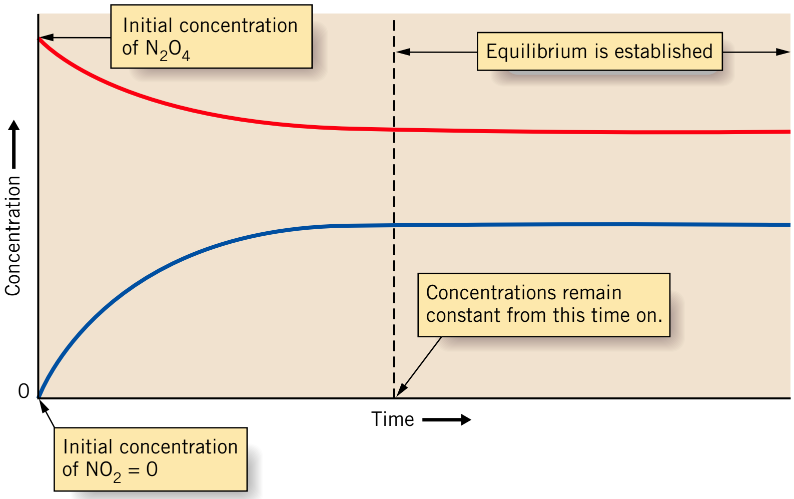


Figure 15.1 | **The approach to equilibrium.** In the decomposition of $N_2O_4(g)$ into $NO_2(g)$, given by the equation $N_2O_4(g) \longrightarrow 2NO_2(g)$, the concentrations of the N_2O_4 and NO_2 change relatively fast at first. As time passes, the concentrations change more and more slowly. When equilibrium is reached, the concentrations of N_2O_4 and NO_2 no longer change with time; they remain constant.

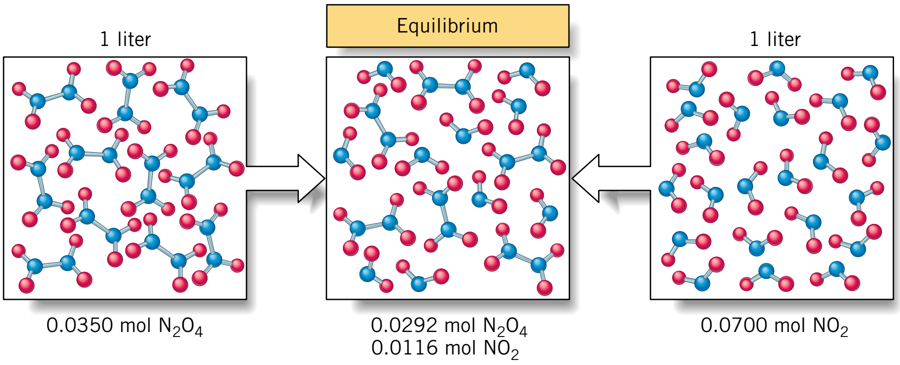


Figure 15.2 | **Reaction reversibility for the equilibrium**

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The same equilibrium composition is reached from either the forward or reverse direction, provided the *overall* system composition is the same.

Approaching Equilibrium from Reactants or Products

One of the interesting (and useful) things about a chemical equilibrium is that the composition of an equilibrium mixture is independent of whether we begin the reaction from the "reactant side" or the "product side." For example, suppose we set up the two experiments shown in Figure 15.2. In the first 1.00 L flask we place 0.0350 mol N_2O_4. Because no NO_2 is present, some N_2O_4 must decompose for the mixture to reach equilibrium, so the reaction in Equation 15.3 will proceed in the forward direction (i.e., from left to right). When equilibrium is reached, we find the concentration of N_2O_4 has dropped to 0.0292 mol L^{-1} and the concentration of NO_2 has increased from zero to 0.0116 mol L^{-1}.

■ Recall that the unit mol L^{-1} (or mol/L) is molarity, *M*.

In the second 1.00 L flask we place 0.0700 mol of NO_2 (*precisely* the amount of NO_2 that would form if 0.0350 mol of N_2O_4—the amount placed in the first flask—decomposed completely). In this second flask there is no N_2O_4 present initially, so NO_2 molecules must combine, following the reverse reaction (right to left) in Equation 15.3, to give enough N_2O_4 to achieve equilibrium. When we measure the concentrations at equilibrium in the second flask, we find, once again, 0.0292 mol L^{-1} of N_2O_4 and 0.0116 mol L^{-1} of NO_2.

■ Stoichiometrically, 0.0700 mol of NO_2 could be formed from 0.0350 mol of N_2O_4, since the ratio of NO_2 to N_2O_4 is 2:1.

We see here that the same equilibrium composition is reached whether we begin with pure NO_2 or pure N_2O_4, as long as the *total* amount of nitrogen and oxygen to be divided between these two substances is the same. Similar observations apply to other chemical systems as well, which leads to the following generalization.

TOOLS

Approach to equilibrium

> For a given *overall* system composition, we always reach the same equilibrium concentrations whether equilibrium is approached from the forward or reverse direction.

There are times when it is very convenient to be able to imagine the approach to equilibrium starting from the product side of the equation.

15.2 | Equilibrium Laws

For any chemical system at equilibrium, there exists a simple, predictable relationship among the molar concentrations of the reactants and products. To study this, let's consider the gaseous reaction of hydrogen with iodine to form hydrogen iodide.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Figure 15.3 shows the results of several experiments measuring equilibrium amounts of each gas, starting with different amounts of the reactants and product in a 10.0 L reaction vessel. When equilibrium is reached, the amounts of H_2, I_2, and HI are different for each experiment, as are their molar concentrations. This isn't particularly surprising, but what is amazing is that the relationship among the concentrations is very simple.

■ The molar concentrations are obtained by dividing the number of moles of each substance by the volume, 10.0 L.

For each experiment in Figure 15.3, if we square the molar concentration of HI at equilibrium and then divide this by the product of the equilibrium molar concentrations

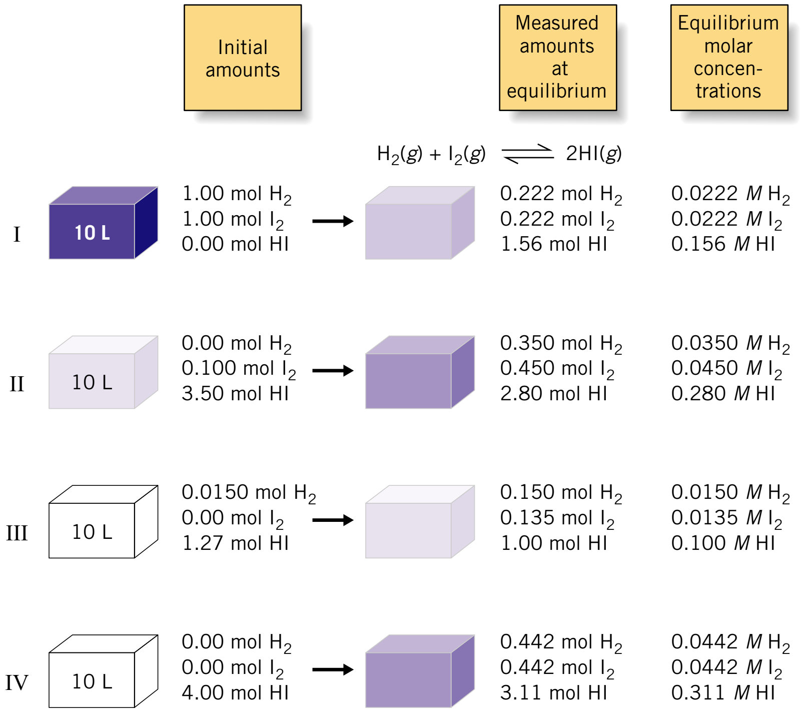

Initial amounts
Measured amounts at equilibrium
Equilibrium molar concen-trations
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
I
10 L
1.00 mol H_2
1.00 mol I_2
0.00 mol HI
0.222 mol H_2
0.222 mol I_2
1.56 mol HI
0.0222 M H_2
0.0222 M I_2
0.156 M HI
II
10 L
0.00 mol H_2
0.100 mol I_2
3.50 mol HI
0.350 mol H_2
0.450 mol I_2
2.80 mol HI
0.0350 M H_2
0.0450 M I_2
0.280 M HI
III
10 L
0.0150 mol H_2
0.00 mol I_2
1.27 mol HI
0.150 mol H_2
0.135 mol I_2
1.00 mol HI
0.0150 M H_2
0.0135 M I_2
0.100 M HI
IV
10 L
0.00 mol H_2
0.00 mol I_2
4.00 mol HI
0.442 mol H_2
0.442 mol I_2
3.11 mol HI
0.0442 M H_2
0.0442 M I_2
0.311 M HI

Figure 15.3 | **Four experiments to study the equilibrium among H_2, I_2, and HI gases.** Different amounts of the reactants and product are placed in a 10.0 L reaction vessel at 440 °C where the gases establish the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g).$$

When equilibrium is reached, different amounts of reactants and products remain in each experiment, which give different equilibrium concentrations.

of H_2 and I_2, we obtain the same numerical value. This is shown in Table 15.1, where we have once again used square brackets around formulas as symbols for molar concentrations.

The fraction used to calculate the values in the last column of Table 15.1,

$$\frac{[HI]^2}{[H_2][I_2]}$$

is called the **mass action expression.**[1] The origin of this term isn't important; just consider it a name we use to refer to this fraction. The numerical value of the mass action expression is called the **reaction quotient**, and is often symbolized by the letter $\boldsymbol{Q}$. For this reaction, we can write

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

This equation applies for any set of H_2, I_2, and HI concentrations, whether we are at equilibrium or not.

In Table 15.1, notice that when H_2, I_2, and HI are in dynamic equilibrium at 440 °C, Q is equal to essentially the same constant value of 49.5. In fact, if we repeated the experiments in Figure 15.3 over and over again starting with different amounts of H_2, I_2, and HI, we would still obtain the same reaction quotient, provided the systems had reached equilibrium and the temperature was 440 °C. Therefore, for this reaction at equilibrium we can write

$$\frac{[HI]^2}{[H_2][I_2]} = 49.5 \qquad \text{(at equilibrium at 440 °C)} \tag{15.4}$$

---

[1] The mass action expression is derived using thermodynamics, which we'll discuss in Chapter 19. Technically, each concentration in the mass action expression should be divided by its value at standard state before inserting it into the expression. This makes the value of any mass action expression unitless. *For substances in solution*, the standard state is an effective molar concentration of 1 M, so we would have to divide each concentration by 1 M (1 mol L^{-1}), which makes no difference in the numerical value of the mass action expression as long as all concentrations are molarities. *For gases*, the standard state is 1 bar, so we would have to divide each gas concentration by its concentration at that pressure, or each gas partial pressure by 1 bar. For simplicity, we'll leave the standard state values out of our mass action expressions. Later we'll see that these values are lumped into the numerical value of the expression.

Table 15.1 Equilibrium Concentrations and the Value of the Mass Action Expression

	Equilibrium Concentrations (mol L^{-1})			
Experiment	$[H_2]$	$[I_2]$	$[HI]$	$\frac{[HI]^2}{[H_2][I_2]}$
I	0.0222	0.0222	0.156	$(0.156)^2/(0.0222)(0.0222) = 49.4$
II	0.0350	0.0450	0.280	$(0.280)^2/(0.0350)(0.0450) = 49.8$
III	0.0150	0.0135	0.100	$(0.100)^2/(0.0150)(0.0135) = 49.4$
IV	0.0442	0.0442	0.311	$(0.311)^2/(0.0442)(0.0442) = 49.5$
				Average = 49.5

This relationship is called the **equilibrium law** for the system. Significantly, it tells us that for a mixture of these three gases to be at equilibrium at 440 °C, the value of the mass action expression (the reaction quotient) must equal 49.5. If the reaction quotient has any other value, then the gases are not in equilibrium at this temperature. The constant 49.5, which characterizes this equilibrium system, is called the **equilibrium constant**. The equilibrium constant is usually symbolized by K_c (we use the subscript **c** because we write the mass action expression using molar concentrations). Thus, we can state the equilibrium law as follows:

$$\frac{[HI]^2}{[H_2][I_2]} = K_c = 49.5 \qquad \text{(at 440 °C)} \tag{15.5}$$

■ Equation 15.5 can be called the equilibrium condition for the reaction of H_2, I_2, and HI at 440 °C.

It is often useful to think of an equilibrium law such as Equation 15.5 as a *condition* that must be met for equilibrium to exist.

TOOLS

Requirement for equilibrium

> For chemical equilibrium to exist in a reaction mixture, the value of the reaction quotient Q must be equal to the equilibrium constant, K_c.

As you may have noticed, we have repeatedly mentioned the temperature when referring to the value of K_c. This is because the value of the equilibrium constant changes when the temperature changes. Thus, if we had performed the experiments in Figure 15.3 at a temperature other than 440 °C, we would have obtained a different value for K_c.

■ In general, it is necessary to specify the temperature when giving a value of K_c, because K_c changes when the temperature changes. For example, for the reaction

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$K_c = 1.78 \times 10^{-3}$ at 800 °C
$K_c = 4.68 \times 10^{-2}$ at 1000 °C
$K_c = 5.67$ at 1500 °C

Homogeneous Equilibria

A **homogeneous reaction** (or **homogeneous equilibrium**) is one in which all of the reactants and products are in the same gas or liquid phase. Equilibria among gases, such as the one described above, are homogeneous because all gases mix freely with each other, so a single phase exists. There are also many equilibria in which reactants and products are dissolved in the same liquid phase, such as an aqueous solution. You will study equilibria in aqueous solutions in Chapters 17 and 18.

An important fact about homogeneous reactions is that the mass action expression and the equilibrium law can *always* be predicted from the coefficients of the balanced chemical equation for the reaction. For example, for the general chemical equation

$$dD + eE \rightleftharpoons fF + gG \tag{15.6}$$

where D, E, F, and G represent chemical formulas and d, e, f, and g are their coefficients, the mass action expression is

$$\frac{[F]^f[G]^g}{[D]^d[E]^e}$$

> *The exponents in the mass action expression are the same as the stoichiometric coefficients in the balanced equation.*

The condition for equilibrium in this reaction is given by the equation

$$\frac{[F]^f[G]^g}{[D]^d[E]^e} = K_c \tag{15.7}$$

where the only concentrations that satisfy the equation are *equilibrium concentrations.*

Notice that in writing the mass action expression the molar concentrations of the products are always placed in the numerator and those of the reactants are always placed in the denominator. Also note that after being raised to appropriate powers the concentration terms are *multiplied*, not added.

■ Notice that even though we cannot predict the *rate law* from the balanced overall equation, we can predict the *equilibrium law.*

TOOLS

The equilibrium law

Example 15.1

Writing the Equilibrium Law

Most of the hydrogen produced in the United States is derived from methane in natural gas, using the forward reaction of the equilibrium

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

What is the equilibrium law for this reaction?

■ **Analysis:** This is a straightforward question, and finding the answer is a task you will repeat many times as you work problems dealing with chemical equilibria.

■ **Assembling the Tools:** The pattern we follow is represented by Equations 15.6 and 15.7, simply substituting formulas and coefficients.

■ **Solution:** The equilibrium law sets the mass action expression equal to the equilibrium constant. To form the mass action expression, we place the concentrations of the products in the numerator and the concentrations of the reactants in the denominator. The coefficients in the balanced chemical equation become exponents on the concentrations. The equilibrium law is

$$\frac{[CO][H_2]^3}{[CH_4][H_2O]} = K_c$$

■ **Is the Answer Reasonable?** Check to see that the products are on top of the fraction and that the reactants are on the bottom. Also check the exponents and be sure they are the same as the coefficients in the balanced chemical equation. Notice that we omit writing the exponent when it is equal to 1.

Practice Exercises

15.1 | The equilibrium law for a reaction is

$$\frac{[NO_2]^4}{[N_2O_3]^2[O_2]} = K_c$$

Write the chemical equation for the equilibrium. (*Hint:* In the equilibrium law, remember where the reactant and product concentrations go and what the exponents mean.)

15.2 | Write the equilibrium law for each of the following:

(a) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

(b) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

The rule that we always write the concentrations of the products in the numerator of the mass action expression and the concentrations of the reactants in the denominator is not required by nature. Rather, it is a convention chemists have agreed to follow. Certainly, if the mass action expression is equal to a constant, its reciprocal is also equal to a constant (let's call it K'_c)

$$\frac{[HI]^2}{[H_2][I_2]} = K_c \qquad \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_c} = K'_c$$

Having a set rule for constructing the mass action expression is very useful; it means we don't have to specify the mass action expression when we give the equilibrium constant for a reaction. For example, suppose we're told that at a particular temperature $K_c = 10.0$ for the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

From the chemical equation, we can write the correct mass action expression and the correct equilibrium law.

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 10.0$$

The balanced chemical equation contains all the information we need to write the equilibrium law.

Manipulating Equilibrium Laws

TOOLS

Manipulating equilibrium equations

Sometimes it is useful to be able to combine chemical equilibria to obtain the equation for some other reaction of interest. In doing this, we perform various operations such as reversing an equation, multiplying the coefficients by some factor, and adding the equations to give the desired equation. In our discussion of thermochemistry, you learned how such manipulations affect ΔH values. Some different rules apply to changes in the mass action expressions and equilibrium constants.

Changing the Direction of an Equilibrium

When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original. You have just seen this in the preceding discussion. As another example, when we reverse the equilibrium

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \qquad K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

we obtain

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad K'_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

The mass action expression for the second reaction is the reciprocal of that for the first, so K'_c equals $1/K_c$.

Multiplying the Coefficients by a Factor

When the coefficients in an equation are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor. For example, suppose we multiply the coefficients of the equation

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \qquad K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

by 2. This gives

$$2PCl_3 + 2Cl_2 \rightleftharpoons 2PCl_5 \qquad K''_c = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2}$$

Comparing mass action expressions, we see that $K''_c = K_c^2$.

Adding Chemical Equilibria

When chemical equilibria are added, their equilibrium constants are multiplied. For example, suppose we add the following two equations.

■ We have numbered the equilibrium constants just to distinguish one from the other.

$$2N_2 + O_2 \rightleftharpoons 2N_2O \qquad K_{c1} = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$2N_2O + 3O_2 \rightleftharpoons 4NO_2 \qquad K_{c2} = \frac{[NO_2]^4}{[N_2O]^2[O_2]^3}$$

$$2N_2 + 4O_2 \rightleftharpoons 4NO_2 \qquad K_{c3} = \frac{[NO_2]^4}{[N_2]^2[O_2]^4}$$

If we multiply the mass action expression for K_{c1} by that for K_{c2}, we obtain the mass action expression for K_{c3}.

$$\frac{\cancel{[N_2O]^2}}{[N_2]^2[O_2]} \times \frac{[NO_2]^4}{\cancel{[N_2O]^2}\,[O_2]^3} = \frac{[NO_2]^4}{[N_2]^2[O_2]^4}$$

Therefore, $K_{c1} \times K_{c2} = K_{c3}$.

Practice Exercises

15.3 | At 25 °C, $K_c = 7.0 \times 10^{25}$ for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the value of K_c for the reaction: $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$? (*Hint:* What do you have to do with the original equation to obtain the new equation?)

15.4 | At 25 °C, the following reactions have the equilibrium constants noted to the right of their equations.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad K_c = 3.3 \times 10^{91}$$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_c = 9.1 \times 10^{80}$$

Use these data to calculate K_c for the reaction

$$H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$$

15.3 | Equilibrium Laws Based on Pressures or Concentrations

When all of the reactants and products are gases, we can formulate mass action expressions in terms of partial pressures as well as molar concentrations. This is possible because the molar concentration of a gas is proportional to its partial pressure (Figure 15.4). If we start with the ideal gas law,

$$PV = nRT$$

and solve for P, we can write the result as

$$P = \left(\frac{n}{V}\right)RT$$

The quantity n/V has units of mol/L and is simply the molar concentration. Therefore, we can write

$$P = (\text{molar concentration}) \times RT \qquad \textbf{(15.8)}$$

■ If you double the number of molecules of a gas per liter without changing the temperature, you double the pressure.

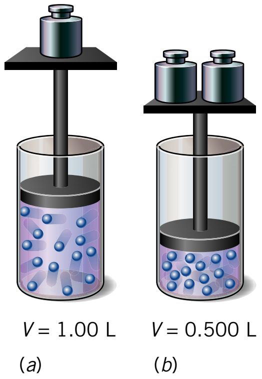


Figure 15.4 | **Molar concentration in a gas is proportional to the pressure.** Going from (a) to (b), we double the pressure, which halves the volume. This packs twice as many molecules into a unit volume, thereby doubling the molar concentration.

This equation applies whether the gas is by itself in a container or part of a mixture. In the case of a gas mixture, P is the partial pressure of the gas.

The relationship expressed in Equation 15.8 lets us write the mass action expression for reactions between gases either in terms of molarities or partial pressures. However, when we make a switch we can't expect the numerical values of the equilibrium constants to be the same, so we use two different symbols for K. When molar concentrations are used, we use the symbol K_c. When partial pressures are used, then $\boldsymbol{K_P}$ is the symbol. For example, the equilibrium law for the reaction of nitrogen with hydrogen to form ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

can be written in either of the following two ways:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = K_c \qquad \left(\begin{array}{l}\text{because molar concentrations are}\\ \text{used in the mass action expression}\end{array}\right)$$

$$\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = K_P \qquad \left(\begin{array}{l}\text{because partial pressures are used}\\ \text{in the mass action expression}\end{array}\right)$$

The equilibrium molar concentrations can be used to calculate K_c, whereas the equilibrium partial pressures can be used to calculate K_P.

Example 15.2
Writing Expressions for K_P

Most of the world's supply of methanol, CH_3OH, is produced by the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

What is the expression for K_P for this equilibrium?

Analysis: This is very similar to Example 15.1, except we're writing the equilibrium law for K_P instead of K_c.

Assembling the Tools: Our tools are the templates given by Equations 15.6 and 15.7, but with partial pressures instead of molar concentrations in the mass action expression.

Solution: In the mass action expression, it's always products over reactants. In this case we use partial pressures raised to powers equal to the coefficients in the balanced equation. The expression for K_P for the reaction is

$$K_P = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2}$$

Is the Answer Reasonable? Check to see that the mass action expression gives products over reactants, and not the other way around. Check each exponent against the coefficients in the balanced chemical equation.

Practice Exercises

15.5 | Write the equilibrium law in terms of partial pressures for the following reaction. (*Hint:* Keep in mind how the mass action expression is written.)

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

15.6 | Using partial pressures, write the equilibrium law for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Relating K_P to K_c

For some reactions K_P is equal to K_c, but for many others the two constants have different values. It is therefore desirable to have a way to calculate one from the other. Converting between K_P and K_c uses the relationship between partial pressure and molarity. Equation 15.8 can be used to change K_P to K_c by substituting

$$(\text{molar concentration}) \times RT$$

for the partial pressure of each gas in the mass action expression for K_P. Similarly, K_c can be changed to K_P by solving Equation 15.8 for the molar concentrations, and then substituting the result, P/RT, into the appropriate expression for K_c. This sounds like a lot of work, and it is. Fortunately, there is a general equation (Equation 15.9), which can be derived from these relationships, that we can use to make the conversions simple.

TOOLS

Converting between K_P and K_c

$$K_P = K_c(RT)^{\Delta n_g} \tag{15.9}$$

In this equation, the value of Δn_g is equal to the change in the *number of moles of gas* in going from the reactants to the products.

$$\Delta n_g = \begin{pmatrix} \text{moles of} \\ \textit{gaseous} \text{ products} \end{pmatrix} - \begin{pmatrix} \text{moles of} \\ \textit{gaseous} \text{ reactants} \end{pmatrix} \tag{15.10}$$

We use the coefficients of the balanced equation for the reaction to calculate the numerical value of Δn_g. For example, the equation

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

tells us that two moles of N_2O are formed when two moles of N_2 and one mole of O_2 react. In other words, two moles of gaseous product are formed from a total of three moles of gaseous reactants. That's a decrease of one mole of gas, so Δn_g for this reaction equals -1.

For some reactions, the value of Δn_g is equal to zero. An example is the decomposition of HI.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

If we take the coefficients to mean moles, there are two moles of gas on each side of the equation, so $\Delta n_g = 0$. Because (RT) raised to the zero power is equal to 1, $K_P = K_c$.

Example 15.3

Converting between K_P and K_c

At 500 °C, the reaction between N_2 and H_2 to form ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_P for this reaction?

■ **Analysis:** Quite clearly, this conversion will require Equation 15.9. However, before we can begin we have to be sure about the units of R and T. When used to stand for temperature, a capital letter T in an equation always means the absolute temperature. Therefore we will have to convert the Celsius temperature to kelvins. Next we must choose an appropriate value for R. Referring back to Equation 15.8, if the partial pressures are expressed in atm and the concentration in mol L^{-1}, the only value of R that includes all of these units (L, mol, atm, and K) is $R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}$, and this is the *only* value of R that can be used in Equation 15.9.

Assembling the Tools: As we've noted, we are going to have to substitute into Equation 15.9.

$$K_P = K_c\,(RT)^{\Delta n_g}$$

To three significant figures, the temperature in kelvins is calculated by the equation: $T_K = T_{°C} + 273$. We also have to calculate Δn_g using Equation 15.10.

$$\Delta n_g = \begin{pmatrix}\text{moles of} \\ \textit{gaseous}\text{ products}\end{pmatrix} - \begin{pmatrix}\text{moles of} \\ \textit{gaseous}\text{ reactants}\end{pmatrix}$$

Solution: Let's start by calculating Δn_g. Interpreting the coefficients in the equation to stand for moles, we have two moles of gaseous products and four moles of gaseous reactants [1 mol $N_2(g)$ and 3 mol $H_2(g)$]. Therefore, $\Delta n_g = (2) - (1 + 3) = -2$.

Assembling the data, then, we have

$$K_c = 6.0 \times 10^{-2} \qquad \Delta n_g = -2$$
$$T = (500 + 273)\text{ K} = 773\text{ K} \qquad R = 0.0821\text{ L atm mol}^{-1}\text{ K}^{-1}$$

Substituting these into the equation for K_P gives

$$\begin{aligned} K_P &= (6.0 \times 10^{-2}) \times [(0.0821) \times (773)]^{-2} \\ &= (6.0 \times 10^{-2}) \times (63.5)^{-2} \\ &= 1.5 \times 10^{-5} \end{aligned}$$

In this case, K_P has a numerical value quite different from that of K_c.

Is the Answer Reasonable? In working these problems, check to be sure you have used the correct value of R and that the temperature is expressed in kelvins. Notice that if Δn_g is negative, as it is in this reaction, the expression $(RT)^{\Delta n_g}$ will be less than one. That should make K_P smaller than K_c, which is consistent with our results.

Practice Exercises

15.7 | Nitrous oxide, N_2O, is a gas used as an anesthetic; it is sometimes called "laughing gas." This compound has a strong tendency to decompose into nitrogen and oxygen following the equation

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$

but the reaction is so slow that the gas appears to be stable at room temperature (25 °C). The decomposition reaction has $K_c = 7.3 \times 10^{34}$. What is the value of K_P for this reaction at 25 °C? (*Hint:* Be careful in calculating Δn_g.)

15.8 | Methanol, CH_3OH, is a promising fuel that can be synthesized from carbon monoxide and hydrogen according to the equation

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

For this reaction at 200 °C, $K_P = 3.8 \times 10^{-2}$. Do you expect K_P to be larger or smaller than K_c? Calculate the value of K_c at this temperature.

15.4 | Equilibrium Laws for Heterogeneous Reactions

Safety-minded cooks keep a box of baking soda nearby because this reaction makes it an excellent fire extinguisher for burning fats or oil. The fire is smothered by the products of the reaction.

When more than one phase exists in a reaction mixture, we call it a **heterogeneous reaction.** A common example is the combustion of charcoal, in which a solid fuel reacts with gaseous oxygen. Another is the thermal decomposition of sodium bicarbonate (baking soda), which occurs when the compound is sprinkled on a fire.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

If $NaHCO_3$ is placed in a sealed container so that no CO_2 or H_2O can escape, the gases and solids come to a heterogeneous equilibrium.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

Following the procedure we developed earlier, we would write the equilibrium law for this reaction as

$$\frac{[Na_2CO_3(s)][H_2O(g)][CO_2(g)]}{[NaHCO_3(s)]^2} = K$$

However, the equilibrium law for reactions involving pure liquids and solids can be written in an even simpler form. This is because the concentration of a pure liquid or solid is unchangeable at a given temperature. *For any pure liquid or solid, the ratio of amount of substance to volume of substance is a constant.* For example, if we had a 1 mole crystal of $NaHCO_3$, it would occupy a volume of 38.9 cm^3. Two moles of $NaHCO_3$ would occupy twice this volume, 77.8 cm^3 (Figure 15.5), but the *ratio* of moles to liters (i.e., the molar concentration) remains the same.

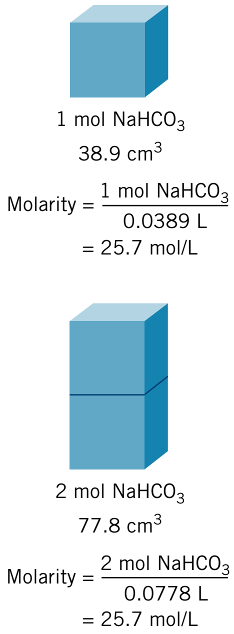

1 mol $NaHCO_3$
38.9 cm^3
Molarity = $\frac{1 \text{ mol } NaHCO_3}{0.0389 \text{ L}}$
= 25.7 mol/L
2 mol $NaHCO_3$
77.8 cm^3
Molarity = $\frac{2 \text{ mol } NaHCO_3}{0.0778 \text{ L}}$
= 25.7 mol/L

Figure 15.5 | **The concentration of a substance in the solid state is a constant.** Doubling the number of moles also doubles the volume, but the *ratio* of moles to volume remains the same.

Similar reasoning shows that the concentration of Na_2CO_3 in pure solid Na_2CO_3 is a constant, too. This means that the equilibrium law now has three constants, K plus two of the concentration terms. It makes sense to combine all of the numerical constants together.

$$[H_2O(g)][CO_2(g)] = \frac{K[NaHCO_3(s)]^2}{[Na_2CO_3(s)]} = K_c$$

Tools

Equilibrium laws for heterogeneous reactions

> The equilibrium law for a heterogeneous reaction is written without concentration terms for pure solids or pure liquids.

Equilibrium constants that are given in tables represent all of the constants combined.[2]

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[2] Thermodynamics handles heterogeneous equilibria in a more elegant way by expressing the mass action expression in terms of "effective concentrations," or **activities**. In doing this, thermodynamics *defines* the *activity* of any pure liquid or solid as equal to 1, which means terms involving such substances drop out of the mass action expression.

Example 15.4
Writing the Equilibrium Law for a Heterogeneous Reaction

The air pollutant sulfur dioxide can be removed from a gas mixture by passing the gases over calcium oxide. The equation is

$$CaO(s) + SO_2(g) \rightleftharpoons CaSO_3(s)$$

Write the equilibrium law for this reaction.

■ **Analysis:** For a heterogeneous equilibrium, we do not include pure solids or pure liquids in the mass action expression. Therefore, we exclude CaO and $CaSO_3$, and include only SO_2.

■ **Assembling the Tools:** Our tool is the method for constructing the equilibrium law.

■ **Solution:** The equilibrium law is simply

$$\frac{1}{[SO_2(g)]} = K_c$$

■ **Is the Answer Reasonable?** There's not much to check here except to review the reasoning, which appears to be okay.

Practice Exercises

15.9 | Write the equilibrium law for the following reaction. (*Hint:* Follow the reasoning above.)

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

15.10 | Write the equilibrium law for each of the following heterogeneous reactions.

(a) $2Hg(l) + Cl_2(g) \rightleftharpoons Hg_2Cl_2(s)$

(b) $Na(s) + H_2O(l) \rightleftharpoons NaOH(aq) + H_2(g)$

(c) Dissolving solid Ag_2CrO_4 in water: $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

(d) $CaCO_3(s) + H_2O(l) + CO_2(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

15.5 | Position of Equilibrium and the Equilibrium Constant

Whether we work with K_P or K_c, a bonus of always writing the mass action expression with the product concentrations in the numerator is that the size of the equilibrium constant gives us a measure of the **position of equilibrium** (how far the reaction proceeds toward completion when equilibrium is reached). For example, the reaction

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

has $K_c = 9.1 \times 10^{80}$ at 25 °C. For an equilibrium between these gases,

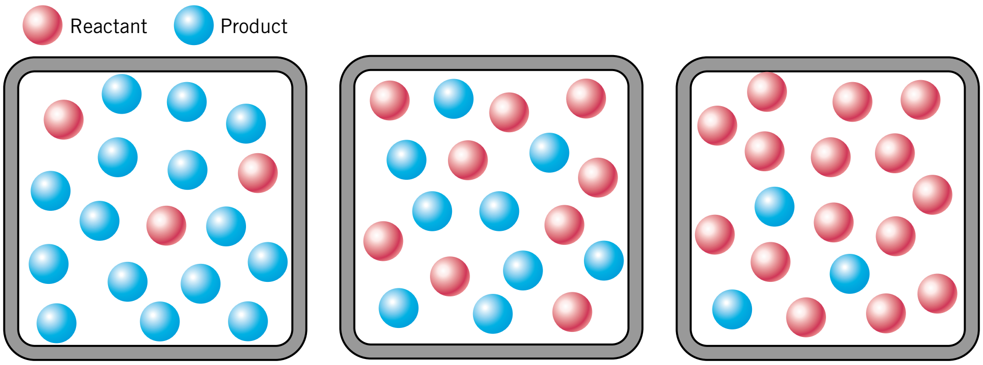
$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{9.1 \times 10^{80}}{1}$$

By writing K_c as a fraction, $(9.1 \times 10^{80})/1$, we see that the numerator of the mass action expression must be enormous compared with the denominator, which means that the concentration of H_2O is huge compared with the concentrations of H_2 and O_2. At equilibrium, therefore, almost all of the hydrogen and oxygen atoms in the system are found in H_2O molecules and very few are present in H_2 and O_2. Thus, the enormous value of K_c tells us that *the position of equilibrium in this reaction lies far toward the right* and that the reaction of H_2 with O_2 goes essentially to completion.

■ Actually, you would need about 200,000 L of water vapor at 25 °C just to find one molecule of O_2 and two molecules of H_2.

The reaction between N_2 and O_2 to give NO,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$



$K >> 1$

The reaction proceeds far toward completion.

$K = 1$

Equilibrium is reached with equal concentrations of reactant and product.

$K << 1$

Hardly any reaction has occurred when equilibrium is reached.

Figure 15.6 | **The position of equilibrium and the magnitude of *K*.** Three views of an equilibrium mixture for reactions of the type

$$\text{reactant} \rightleftharpoons \text{product}$$

If $K >> 1$, the concentration of product is much larger than the concentration of reactant. The two concentrations are equal if $K = 1$, and the concentration of the product is much smaller than that of the reactant if $K << 1$.

has a very small equilibrium constant; $K_c = 4.8 \times 10^{-31}$ at 25 °C. The equilibrium law for the reaction is

$$\frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]} = 4.8 \times 10^{-31} = \frac{4.8}{10^{31}}$$

Here the denominator is huge compared with the numerator, so the concentrations of N_2 and O_2 must be very much larger than the concentration of NO. This means that in a mixture of N_2 and O_2 at this temperature, the amount of NO that is formed is negligible. The reaction hardly proceeds at all toward completion before equilibrium is reached, and *the position of equilibrium lies far toward the left.*

■ In air at 25 °C, the equilibrium concentration of NO *should be* about 10^{-17} mol/L. It is usually higher because NO is formed in various reactions, such as those responsible for air pollution caused by automobiles.

The relationship between the equilibrium constant and the position of equilibrium can thus be summarized as follows (also see Figure 15.6):

When *K* is very large	The reaction proceeds far toward completion. The position of equilibrium lies far to the right, toward the products.
When $K \approx 1$	The concentrations of reactants and products are nearly the same at equilibrium. The position of equilibrium lies approximately midway between reactants and products.
When *K* is very small	Extremely small amounts of products are formed. The position of equilibrium lies far to the left, toward the reactants.

Significance of the magnitude of *K*

Notice that we have omitted the subscript for *K* in this summary. The same qualitative predictions about the extent of reaction apply whether we use K_P or K_c.

One of the ways that we can use equilibrium constants is to compare the extents to which two or more reactions proceed to completion. Take care in making such comparisons, however, because unless the values of *K* are greatly different, the comparison is valid only if both reactions have the same number of reactant and product molecules appearing in their balanced chemical equations.

Practice Exercises

15.11 | Suppose a mixture contained equal concentrations of H_2, Br_2, and HBr. Given that the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ has $K_c = 1.4 \times 10^{-21}$, will the reaction proceed to the left or right in order to reach equilibrium? (*Hint:* In the mass action expression for this reaction, how should the size of the numerator compare with that of the denominator when the system reaches equilibrium?)

15.12 | Arrange the following reactions in order of their increasing tendency to proceed toward completion?

(a) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	$K_c = 1.4 \times 10^{-21}$
(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$	$K_c = 2.1 \times 10^{30}$
(c) $2BrCl \rightleftharpoons Br_2 + Cl_2$ (in CCl_4 solution)	$K_c = 0.145$

15.6 | Equilibrium and Le Châtelier's Principle

In Section 15.8 you will see that it is possible to perform calculations that tell us what the composition of an equilibrium system is. However, many times we really don't need to know exactly what the equilibrium concentrations are. Instead, we may want to know what actions we should take to control the relative amounts of the reactants or products at equilibrium. For instance, if we were designing gasoline engines, we would like to know what could be done to minimize the formation of nitrogen oxide pollutants. Or, if we were preparing ammonia, NH_3, by the reaction of N_2 with H_2, we might want to know how to maximize the yield of NH_3.

Le Châtelier's principle, introduced in Chapter 12, provides us with the means for making qualitative predictions about changes in chemical equilibria. It does this in much the same way that it allows us to predict the effects of outside influences on equilibria that involve physical changes, such as liquid–vapor equilibria. Recall that **Le Châtelier's principle** states that *if an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium.* Let's examine the kinds of "outside influences" that affect chemical equilibria.

Adding or Removing a Reactant or Product

■ Recall that the reaction quotient, *Q*, is the numerical value of the mass action expression.

When a system is at equilibrium, the reaction quotient *Q* is equal to *K*. For a homogeneous system, if we add or remove some of a reactant or product, the value of *Q* changes, which means it no longer equals *K* and the system is no longer at equilibrium. In other words, the equilibrium has been upset, and according to Le Châtelier's principle the system should change in a direction that opposes the disturbance we've introduced. If we've added a substance, the reaction should proceed in a direction to remove some of it; if we've removed a substance, the reaction should proceed in a direction to replace it.

As an example, let's study the following equilibrium between two *complex ions* of copper.

■ $Cu(H_2O)_4^{2+}$ and $CuCl_4^{2-}$ are called ***complex ions***. Some of the interesting properties of complex ions of metals are discussed in Chapter 22.

$$\underset{\text{blue}}{Cu(H_2O)_4^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{yellow}}{CuCl_4^{2-}(aq)} + 4H_2O(l)$$

As noted, $Cu(H_2O)_4^{2+}$ is blue and $CuCl_4^{2-}$ is yellow. Mixtures of the two have an intermediate color and therefore appear blue-green, as illustrated in Figure 15.7, center.

Suppose we add chloride ion to an equilibrium mixture of these copper ions. The system can remove some Cl^- by reacting it with $Cu(H_2O)_4^{2+}$. This gives more $CuCl_4^{2-}$ (Figure 15.7, right), and we say that the equilibrium has "shifted to the right" or "shifted toward the products." In the new position of equilibrium, there is less $Cu(H_2O)_4^{2+}$ and more $CuCl_4^{2-}$ and uncombined H_2O. There is also more Cl^-, because not all that we add reacts. In other words, in this new position of equilibrium, *all* the concentrations have changed in a way that causes *Q* to become equal to K_c. Similarly, the position of equilibrium is shifted to the left when we add water to the mixture (Figure 15.7, left). The system is able to get rid of some of the H_2O by reaction with $CuCl_4^{2-}$, so more of the blue $Cu(H_2O)_4^{2+}$ is formed.

■ The reaction shifts in a direction that will remove a substance that's been added or replace a substance that's been removed.

If we were able to remove a reactant or product, the position of equilibrium would also be changed. For example, if we add Ag^+ to a solution that contains both copper ions in equilibrium, we see an enhancement of the blue color.

$$\begin{array}{c}\underset{\text{blue}}{Cu(H_2O)_4^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{yellow}}{CuCl_4^{2-}(aq)} + 4H_2O \\ \Downarrow \\ Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)\end{array}$$

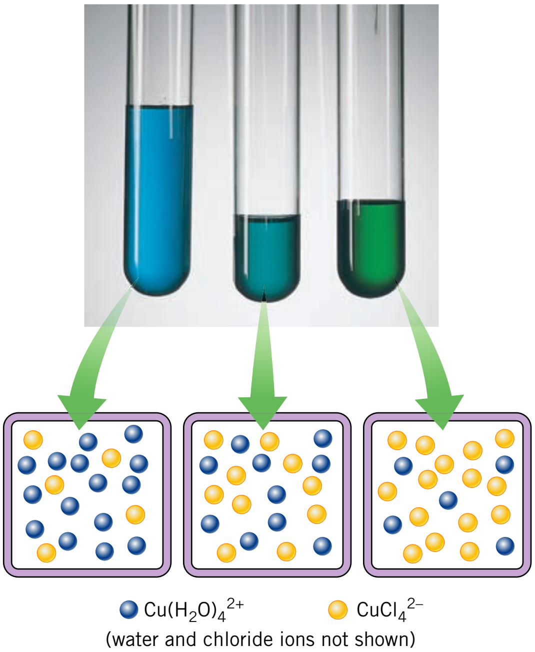


Figure 15.7 | **The effect of concentration changes on the position of equilibrium.** The solution in the center contains a mixture of blue $Cu(H_2O)_4^{2+}$ and yellow $CuCl_4^{2-}$, so it has a blue-green color. At the right, some of the same solution after the addition of concentrated HCl. It has a more pronounced green color because the equilibrium is shifted toward $CuCl_4^{2-}$. At the left is some of the original solution after the addition of water. It is blue because the equilibrium has shifted toward $Cu(H_2O)_4^{2+}$. *(Michael Watson)*

As the Ag^+ reacts with Cl^- to form insoluble AgCl in the second reaction, the equilibrium in the first reaction shifts to the left to replace some of the Cl^-, which also produces more blue $Cu(H_2O)_4^{2+}$. The position of equilibrium shifts to replace the substance that is removed.

> The position of equilibrium shifts in a way to remove reactants or products that have been added, or to replace reactants or products that have been removed.

TOOLS

Le Châtelier's principle; adding or removing a reactant or product

Changing the Volume of a Gaseous Equilibrium

Changing the volume of a mixture of reacting gases changes molar concentrations and partial pressures, so we would expect volume changes to have some effect on the position of equilibrium. Let's consider the equilibrium involved in the industrial synthesis of ammonia, which was described in the opening photo of this chapter and is the subject of *Chemistry Outside the Classroom 15.1*.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

If we reduce the volume of the reaction mixture, we cause the pressure to increase. The system can counteract the pressure increase if it is able to produce fewer molecules of gas, because fewer molecules exert a lower pressure. For the reaction above, forming more ammonia does just that. When the reaction proceeds to the right, two NH_3 molecules appear when four molecules (one N_2 and three H_2) disappear. Therefore, this equilibrium is shifted to the right when the volume of the reaction mixture is reduced.

Now let's look at the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If this reaction proceeds in either direction, there is no change in the number of molecules of gas. This reaction, therefore, cannot respond to pressure changes, so changing the volume of the reaction vessel has virtually no effect on the equilibrium.

The simplest way to analyze the effects of a volume change on an equilibrium system involving gases is to count the number of molecules of *gaseous* substances on both sides of the equation.

CHEMISTRY OUTSIDE THE CLASSROOM 15.1

The Haber Process: Feeding Earth's Population

In the popular press, "chemistry" is often given a "bloody nose." Rarely is it mentioned that without the chemical industry, widespread famine would exist today across the world. This is because nearly one-third of the earth's human population is sustained by fertilizers generated from ammonia produced by the reaction of H_2 with N_2 in an industrial process known as the Haber process (also called the Haber–Bosch process).

At room temperature and pressure, nitrogen has little tendency to react with anything. The strong triple bond in the N_2 molecule causes any reaction that involves the breaking of the $N\equiv N$ bond to have a very high activation energy, which makes the reaction extremely slow. Making the reaction between H_2 and N_2 industrially viable requires extreme conditions of pressure and temperature. In the summer of 1909, Fritz Haber demonstrated how to overcome these obstacles, and Carl Bosch later scaled up the process to industrial size. Both Haber and Bosch were later awarded Nobel Prizes for their work.

In a modern ammonia synthesis plant, hydrogen is obtained from natural gas, which is composed chiefly of methane, CH_4. Methane is reacted with steam over a nickel oxide catalyst.

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

The net result is that methane and steam are converted to hydrogen gas and carbon dioxide. Nitrogen for the Haber process is obtained from air, where it is present at a level of 78%.

The final stage of the process is to combine hydrogen and nitrogen over an iron oxide catalyst.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92.4 \text{ kJ mol}^{-1}$$

High pressures in the range of 150–250 atm are used to help force the position of equilibrium to the right. High temperatures (300–500 °C) are also used, even though they tend to shift the position of equilibrium away from ammonia. This is necessary to make the catalyst effective and make the reaction proceed at an acceptable rate. Under these conditions, one pass over the catalyst bed produces a yield of only about 15%, but the mixture is passed over multiple catalyst beds, with cooling between passes to remove NH_3. Any unreacted gases are recycled, so eventually a total yield of nearly 98% is achieved.

Ammonia itself can be used as a fertilizer by injecting it directly into the ground, where it is captured by moisture in the soil (Figure 1). The gas also serves as a raw material for the production of nitrates and nitrites, which can be isolated as potassium or ammonium salts. The latter are solids that can be incorporated with other necessary plant nutrients to produce more complete fertilizers.

Figure 1 A farmer operates machinery that injects ammonia gas directly into the soil, where it will act as a fertilizer. *Doug Martin/Photo Researchers*

TOOLS

Le Châtelier's principle; changing the volume of a gaseous equilibrium

Reducing the volume of a gaseous reaction mixture causes the position of equilibrium to shift in a direction that decreases the number of molecules of gas. No change in the equilibrium will occur if a volume change cannot affect the number of molecules of gas.

As a final note here, *moderate pressure changes have negligible effects on reactions involving only liquids or solids*. Substances in these states are virtually incompressible, and reactions involving them have no way to counteract pressure changes.

Changing the Temperature

To change the temperature of an equilibrium system, heat is either added or removed. For example, the decomposition of $N_2O_4(g)$ into $NO_2(g)$ discussed in Section 15.1 is endothermic in the forward direction, with $\Delta H^\circ = +57.9$ kJ.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H^\circ = +57.9 \text{ kJ}$$

If we add heat to raise the temperature of the equilibrium mixture, the position of equilibrium will shift in the direction that absorbs heat. Because the reaction from left to right is endothermic, the position of equilibrium will shift to the right. This increases the concentration of NO_2 and decreases the concentration of N_2O_4.

Sometimes it's easier to analyze the effect if we include energy in the equation. For this reaction, heat is absorbed in the forward direction, so we include heat as a reactant.

$$\text{Heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Adding a reactant drives the reaction in the forward direction, with heat behaving like any other reactant in this case.

Lowering the temperature by removing heat from an equilibrium system has the opposite effect from adding heat. Such a disturbance to the equilibrium promotes an exothermic change, which partially replaces the heat removed. In the preceding reaction, the reaction from right to left is exothermic, so removing heat from the system shifts the equilibrium position to the left. This causes the concentration of N_2O_4 to increase and the concentration of NO_2 to decrease.

> Increasing the temperature shifts a reaction in a direction that produces an endothermic (heat-absorbing) change.
>
> Decreasing the temperature shifts a reaction in a direction that produces an exothermic (heat-releasing) change.

TOOLS

Le Châtelier's principle; raising or lowering the temperature

This gives us a way to experimentally determine whether a reaction is exothermic or endothermic, without using a thermometer. Earlier we described the equilibrium involving complex ions of copper. The effect of temperature on this equilibrium is demonstrated in Figure 15.8. When the reaction mixture is heated, we see from the color change that the equilibrium shifts toward the products. Therefore, the reaction must be endothermic.

■ When heat is added to an equilibrium mixture, it is added to all of the substances present (reactants *and* products). As the system returns to equilibrium, the net reaction that occurs is the one that is endothermic.

Effect of Temperature Changes on *K* for a Reaction

Changes in concentrations or volume can shift the position of equilibrium, but *they do not change the equilibrium constant.* Changing the temperature, however, causes the position of equilibrium to shift because it changes the value of *K*. The enthalpy change of the reaction is the critical factor. Consider, for example, the equilibrium for the formation of ammonia.

■ Temperature is the only factor that can change *K* for a given reaction.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -46.19 \text{ kJ}$$

$$\frac{[NH_3]^2}{[H_2]^3[N_2]} = K_c$$

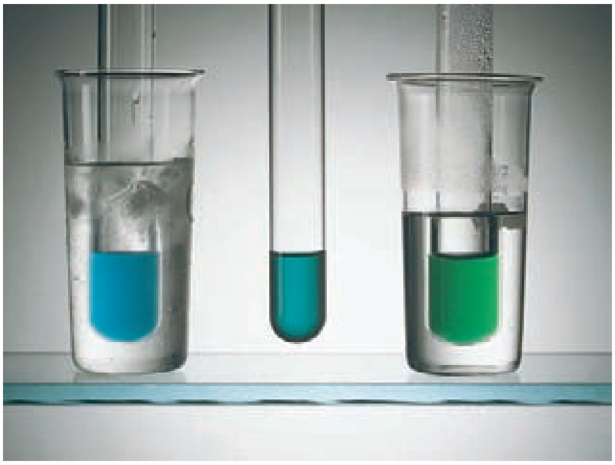


Figure 15.8 | **The effect of temperature on the equilibrium**

$$\mathbf{Cu(H_2O)_4^{2+} + 4Cl^- \rightleftharpoons CuCl_4^{2-} + 4H_2O}$$

In the center is an equilibrium mixture of the two complex ions. When the solution is cooled in ice (left), the equilibrium shifts toward the blue $Cu(H_2O)_4^{2+}$. When heated in boiling water (right), the equilibrium shifts toward $CuCl_4^{2-}$. This behavior indicates that the reaction is endothermic in the forward direction. *(Michael Watson)*

Because the reaction is exothermic, increasing the temperature shifts the equilibrium to the left. When equilibrium is restored, the concentration of NH_3 has decreased and the concentrations of N_2 and H_2 have increased. Therefore, the numerator of the mass action expression has become *smaller* and the denominator *larger*. This gives a smaller reaction quotient and therefore a smaller value of K_c.

■ We'll see how to quantitatively relate *K* and temperature in Chapter 19.

Le Châtelier's principle; changing temperature changes *K*

> Increasing the temperature of an exothermic reaction makes its equilibrium constant smaller.
>
> Increasing the temperature of an endothermic reaction makes its equilibrium constant larger.

Catalysts and the Position of Equilibrium

Recall that catalysts are substances that affect the speeds of chemical reactions without actually being used up. However, *catalysts do not affect the position of equilibrium in a system.* The catalyst's only effect is to bring the system to equilibrium faster.

■ Catalysts don't appear in the chemical equation for a reaction, so they don't appear in the mass action expression, either.

Pressure Changes Caused by Adding an Inert Gas at Constant Volume

A change in volume is not the only way to change the pressure in an equilibrium system of gaseous reactants and products. The pressure can also be changed by keeping the volume the same and adding another gas. If this gas cannot react with any of the gases already present (i.e., if the added gas is *inert* toward the substances in equilibrium), the concentrations and partial pressures of the reactants and products won't change. They will continue to satisfy the equilibrium law and the reaction quotient will continue to equal K_c, so there will be no change in the position of equilibrium.

Example 15.5

Application of Le Châtelier's Principle

The reaction $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ is endothermic with $K_c = 5.67$ at 1500 °C. How will the amount of $CO(g)$ at equilibrium be affected by (a) adding more $H_2O(g)$, (b) lowering the pressure by increasing the volume of the container, (c) raising the temperature of the reaction mixture, and (d) adding a catalyst to the system? Which of these will change the equilibrium constant and in which direction (increase or decrease) will K_c change?

■ **Analysis:** The problem asks us to predict the effects of various changes on the position of equilibrium, which is the clue that tells us the problem requires application of Le Châtelier's principle.

■ **Assembling the Tools:** Each of these kinds of disturbances was described in the preceding discussion, and the tools to deal with them are found in the statements in that discussion. We simply select the tool according to the type of disturbance involved.

■ **Solution:** (a) Adding H_2O will cause the equilibrium to shift to the right, in a direction that will consume some of the added H_2O. The amount of CO will increase.

(b) When the pressure in the system drops, the system responds by producing more molecules of gas, which will tend to raise the pressure and partially offset the change. If the reaction goes from left to right, we use up two molecules (one CH_4 and one H_2O) and form four molecules (one CO and three H_2). This yields a net increase in the number of molecules, so some CH_4 and H_2O react and the amount of CO at equilibrium will increase.

(c) Because the reaction is endothermic, we write the equation showing heat as a reactant:

$$\text{Heat} + CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Raising the temperature is accomplished by adding heat, so the system will respond by absorbing heat. This means that the equilibrium will shift to the right and the amount of CO at equilibrium will increase.

(d) A catalyst causes a reaction to reach equilibrium more quickly, but it has no effect on the position of chemical equilibrium. Therefore, the amount of CO at equilibrium will not be affected.

Finally, the *only* change that alters K is the temperature change. Raising the temperature (adding heat) will increase K_c for this endothermic reaction.

■ **Are the Answers Reasonable?** There's not much we can do here other than review our reasoning. Doing so will reveal we've answered the questions correctly.

Practice Exercises

15.13 | Consider the equilibrium $PCl_5(g) + 4H_2O(g) \rightleftharpoons H_3PO_4(l) + 5HCl(g)$. How will the amount of H_3PO_4 at equilibrium be affected by decreasing the volume of the container holding the reaction mixture? (*Hint:* Notice that this is a heterogeneous equilibrium.)

15.14 | Consider the equilibrium $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, for which $\Delta H° = -88$ kJ. How will the amount of Cl_2 at equilibrium be affected by (a) adding PCl_3, (b) adding PCl_5, (c) raising the temperature, and (d) decreasing the volume of the container? How (if at all) will each of these changes affect K_P for the reaction?

15.7 | Calculating Equilibrium Constants

In Section 15.5 you learned that the magnitude of an equilibrium constant gives us some feel for the extent to which the reaction proceeds at equilibrium. Sometimes, however, it is necessary to have more than merely a qualitative knowledge of equilibrium concentrations. This requires that we be able to use the equilibrium law for purposes of calculation.

Equilibrium calculations for gaseous reactions can be performed using either K_P or K_c, but for reactions in solution we must use K_c. Whether we deal with concentrations or partial pressures, however, the same basic principles apply.

Overall, we can divide equilibrium calculations into two main categories:

1. Calculating equilibrium constants from known equilibrium concentrations or partial pressures.
2. Calculating one or more equilibrium concentrations or partial pressures using the known value of K_c or K_P.

In this section we will study how to calculate equilibrium constants. To keep things as simple as possible, we will stick to working problems involving K_c and molar concentrations.

One way to determine the value of K_c is to carry out the reaction, measure the concentrations of reactants and products after equilibrium has been reached, and then use the equilibrium values in the equilibrium law to compute K_c. As an example, let's look again at the decomposition of N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In Section 15.2, we saw that if 0.0350 mol of N_2O_4 is placed into a 1.00 liter flask at 25 °C, the concentrations of N_2O_4 and NO_2 at equilibrium are

$$[N_2O_4] = 0.0292 \text{ mol/L}$$
$$[NO_2] = 0.0116 \text{ mol/L}$$

To calculate K_c for the reaction, we substitute the equilibrium concentrations into the mass action expression of the equilibrium law.

$$\frac{[NO_2]^2}{[N_2O_4]} = K_c$$
$$\frac{(0.0116)^2}{(0.0292)} = K_c$$

Performing the arithmetic gives

$$K_c = 4.61 \times 10^{-3}$$

Concentration Tables

Concentration table

Only rarely are we given all the equilibrium concentrations required to calculate the equilibrium constant. Usually, we have information about the composition of a reaction mixture when it is first prepared, as well as some additional data that we can use to figure out what the equilibrium concentrations are. To help organize our thinking, our tool will be a **concentration table** that we will set up beneath the chemical equation. In this table we keep track of the concentrations of the substances involved in the reaction as it proceeds toward equilibrium. Normally the table has the same number of data columns as there are substances in the equilibrium equation. The table has three rows, which we label *Initial Concentrations, Changes in Concentrations*, and *Equilibrium Concentrations*. Entries in the table are either numbers with units of molar concentration (mol L^{-1}) or variables (e.g., x) that represent molar concentrations. Let's look at how the data for each row are obtained.

Initial Concentrations

The initial concentrations are those present in the reaction mixture when it's prepared; *we imagine that no reaction occurs until everything is mixed.* Often, the statement of a problem will give the initial molar concentrations, and these are then entered into the table under the appropriate formulas. In other cases, the mass or number of moles of reactants or products dissolved in a specified volume are given and we must then calculate the molar concentrations. *If the initial amount or concentration of a reactant or product is not mentioned in the problem, we will assume none was added to the reaction mixture initially, so its initial concentration is entered as zero.*

■ Remember, all entries in the concentration table must be molarities. If you use moles instead, you may end up with incorrect answers.

Changes in Concentrations

If the reaction mixture is not at equilibrium when it's prepared, the chemical reaction must occur (either to the left or right) to bring the system to equilibrium. When this happens, the concentrations change. We will use a positive sign to indicate that a concentration increases and a negative sign to show a decrease in concentration.

The changes in concentrations ***always*** *occur in the same ratio as the coefficients in the balanced equation.* For example, if we were dealing with the equilibrium

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

and found that the $N_2(g)$ concentration decreases by 0.10 *M* during the approach to equilibrium, the entries in the "change" row would be as follows:

$$\begin{array}{lccccc} & 3H_2(g) & + & N_2(g) & \rightleftharpoons & 2NH_3(g) \\ \text{Changes in Concentrations:} & -3 \times (0.10\ M) & & -1 \times (0.10\ M) & & +2 \times (0.10\ M) \\ & \downarrow & & \downarrow & & \downarrow \\ & -0.30\ M & & -0.10\ M & & +0.20\ M \end{array}$$

In constructing the "change" row, *be sure that the reactant concentrations all change in the same direction and that the product concentrations all change in the opposite direction*. If the concentrations of the reactants decrease, all the entries for the reactants in the "change" row should have a minus sign, and all the entries for the products should be positive. In this example, N_2 reacts with H_2 (so their concentrations both decrease) and form NH_3 (so its concentration increases).

In Section 15.8, where we will be trying to find equilibrium concentrations from K_c and initial concentrations, our goal will be to find numerical values for the quantities in the change row. These quantities will be unknowns and will be represented symbolically by variables.

Equilibrium Concentrations

These are the concentrations of the reactants and products when the system finally reaches equilibrium. We obtain them by adding the changes in concentrations to the initial concentrations.

$$\begin{pmatrix}\text{initial} \\ \text{concentration}\end{pmatrix} + \begin{pmatrix}\text{change in} \\ \text{concentration}\end{pmatrix} = \begin{pmatrix}\text{equilibrium} \\ \text{concentration}\end{pmatrix}$$

The equilibrium concentrations are the only quantities that satisfy the equilibrium law. In this section we will use the numerical values in the last row to calculate K_c.

The concentration table is one of our most useful tools for analyzing and setting up equilibrium problems. As you will see, we will use it in almost every problem. The following example illustrates how we can use it in calculating an equilibrium constant.

Example 15.6

Calculating K_c from Equilibrium Concentrations

At a certain temperature, a mixture of H_2 and I_2 was prepared by placing 0.200 mol of H_2 and 0.200 mol of I_2 into a 2.00 liter flask. After a period of time the following equilibrium was established:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The purple color of the I_2 vapor was used to monitor the reaction, and from the decreased intensity of the purple color it was determined that, at equilibrium, the I_2 concentration had dropped to 0.020 mol L^{-1}. What is the value of K_c for this reaction at this temperature?

■ **Analysis:** The first step in *any* equilibrium problem is to write the balanced chemical equation and the related equilibrium law. The equation is already given, and the equilibrium law corresponding to it is

$$\frac{[HI]^2}{[H_2][I_2]} = K_c$$

To calculate the value of K_c we must substitute the *equilibrium concentrations* of H_2, I_2, and HI into the mass action expression. But what are they? We have been given only one directly, the value of $[I_2]$. To obtain the others, we have to do some chemical reasoning.

Assembling the Tools: The principal tool to solve this problem will be a concentration table, constructed following the procedure described previously. Once we've filled in the last row of the table, we can substitute the values for the equilibrium concentrations into the next tool, the equilibrium law, and calculate K_c. Because the table must contain molar concentrations, another tool we will apply is the definition of molarity.

Solution: The first step is to enter the data given in the statement of the problem. As noted above, the entries must be molar concentrations, but we've been given moles and the volume of the container. Therefore, for the initial concentrations we have to calculate the ratio of moles to liters for both the H_2 and I_2, (0.200 mol/2.00 L) = 0.100 *M*. Because no HI was placed into the reaction mixture, its initial concentration is set to zero. These quantities are shown in colored type in the first row. The problem statement also gives us the equilibrium concentration of I_2, so we enter this in the table in the last row (also shown in colored type). The values in regular type are then derived as described below.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial concentrations (*M*)	**0.100**		**0.100**		**0.000**
Changes in concentrations (*M*)	−0.080		−0.080		+2(0.080)
Equilibrium concentrations (*M*)	0.020		**0.020**		0.160

The changes in concentrations are controlled by the stoichiometry of the reaction. If we can find one of the changes, we can calculate the others from it.

Changes in Concentrations

We have been given both the initial and equilibrium concentrations of I_2, so by difference we can calculate the change for I_2 (−0.080 *M*). The other changes are then calculated from the mole ratios specified by the coefficients of the balanced equation. Because H_2 and I_2 have the same coefficients (i.e., 1), their changes are equal. The coefficient of HI is 2, so its change must be twice that of I_2. Reactant concentrations are decreasing, so their changes are negative; the product concentration increases, so its change is positive.

Equilibrium Concentrations

For H_2 and HI, we just add the change to the initial value.

The hard work has now been done. We substitute the equilibrium concentrations from the last row of the table into the mass action expression and calculate K_c.

$$K_c = \frac{(0.160)^2}{(0.020)(0.020)}$$
$$= 64$$

Is the Answer Reasonable? First, carefully examine the equilibrium law. As always, products must be placed in the numerator and reactants in the denominator. Be sure that each exponent corresponds to the correct coefficient in the balanced chemical equation.

Next, check the concentration table to be sure all entries are molar concentrations. Note that the initial concentration of HI is zero. The change for HI must be positive, because the HI concentration cannot become smaller than zero. The positive value in the table agrees with this assessment. Notice, also, that the changes for both reactants have the same sign, which is opposite that of the product. *This relationship among the signs of the changes is always true and serves as a useful check when you construct a concentration table.*

Finally, we can check to be sure we've entered each of the equilibrium concentrations into the mass action expression correctly. At this point we can be confident we've set up the problem correctly. To be sure of the answer, redo the calculation on your calculator.

Practice Exercises

15.15 | In a particular experiment, it was found that when $O_2(g)$ and $CO(g)$ were mixed and allowed to react according to the equation

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

the O_2 concentration had decreased by 0.030 mol L^{-1} when the reaction reached equilibrium. How had the concentrations of CO and CO_2 changed? (*Hint:* How are the changes in concentrations related to one another as the reaction approaches equilibrium?)

15.16 | An equilibrium was established for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

at 500 °C. (This is an industrially important reaction for the preparation of hydrogen.) At equilibrium, the following concentrations were found in the reaction vessel: $[CO] = 0.180\ M$, $[H_2O] = 0.0411\ M$, $[CO_2] = 0.150\ M$, and $[H_2] = 0.200\ M$. What is the value of K_c for this reaction?

15.17 | A student placed 0.200 mol of $PCl_3(g)$ and 0.100 mol of $Cl_2(g)$ into a 1.00 liter container at 250 °C. After the reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

came to equilibrium it was found that the flask contained 0.120 mol of PCl_3.

(a) What were the initial concentrations of the reactants and product?
(b) By how much had the concentrations changed when the reaction reached equilibrium?
(c) What were the equilibrium concentrations?
(d) What is the value of K_c for this reaction at this temperature?

15.8 | Using Equilibrium Constants to Calculate Concentrations

In the simplest calculation of this type, all but one of the equilibrium concentrations are known, as illustrated in Example 15.7.

Example 15.7
Using K_c to Calculate Concentrations at Equilibrium

The reversible reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

has been used as a commercial source of hydrogen. At 1500 °C, $K_c = 5.67$ and an equilibrium mixture of these gases was found to have the following concentrations: $[CO] = 0.300\ M$, $[H_2] = 0.800\ M$, and $[CH_4] = 0.400\ M$. At 1500 °C, what was the equilibrium concentration of $H_2O(g)$ in the mixture?

■ **Analysis:** We have all of the equilibrium concentrations except one. Because the equilibrium concentrations are related to each other by the equilibrium law, we should be able to substitute values and solve for $[H_2O]$.

■ **Assembling the Tools:** In solving any equilibrium problem, the tools we need are the balanced chemical equation and the equilibrium law. We already have the equation, so we use it to write

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

(By now you should be familiar with the procedure for doing this. If not, review Section 15.2.)

Solution: We substitute the values given in the statement of the problem into the equilibrium law and solve for the unknown quantity.

$$5.67 = \frac{(0.300)(0.800)^3}{(0.400)[H_2O]}$$

Solving for $[H_2O]$ gives

$$[H_2O] = \frac{(0.300)(0.800)^3}{(0.400)(5.67)} = \frac{0.154}{2.27} = 0.0678\ M$$

Is the Answer Reasonable? *We can always check problems of this kind by substituting all of the equilibrium concentrations into the mass action expression to see if the value of Q we get equals K_c.* Let's do this.

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(0.300)(0.800)^3}{(0.400)(0.0678)} = 5.66$$

Rounding off the H_2O concentration caused a slight error, but Q is so close to K_c that we can be sure we've solved the problem correctly.

Practice Exercises

15.18 | The decomposition of N_2O_4 at 25 °C,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

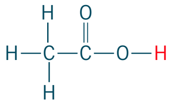
has $K_c = 4.61 \times 10^{-3}$. A 2.00 L vessel contained 0.0466 mol N_2O_4 at equilibrium. What was the concentration of NO_2 in the vessel? (*Hint:* What was the concentration of N_2O_4 in the container at equilibrium?)

15.19 | Ethyl ethanoate (commonly called ethyl acetate), $CH_3CO_2C_2H_5$, is an important solvent used in nail polish remover, lacquers, adhesives, the manufacture of plastics, and even as a food flavoring. It is produced from acetic acid and ethanol by the reaction

$$\underset{\substack{\text{ethanoic acid}\\\text{(acetic acid)}}}{CH_3CO_2H} + \underset{\text{ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\substack{\text{ethyl ethanoate}\\\text{(ethyl acetate)}}}{CH_3CO_2C_2H_5} + H_2O$$

At 25 °C, $K_c = 4.10$ for this reaction. In a reaction mixture, the following equilibrium concentrations were observed: $[CH_3CO_2H] = 0.210\ M$, $[H_2O] = 0.00850\ M$, and $[CH_3CO_2C_2H_5] = 0.910\ M$. What was the concentration of C_2H_5OH in the mixture?

Recall that acetic acid has the structure



where the hydrogen released by ionization is indicated in red. The formula of the acid is written either as CH_3CO_2H (which emphasizes its molecular structure) or as $HC_2H_3O_2$ (which emphasizes that the acid is monoprotic).

Using K_c and Initial Concentrations

A more complex type of calculation involves the use of initial concentrations and K_c to compute equilibrium concentrations. Although some of these problems can be so complicated that a computer is needed to solve them, we can learn the general principles involved by working on simple calculations. Even these, however, require a little applied algebra. This is where the concentration table can be especially helpful.

Example 15.8
Using K_c to Calculate Equilibrium Concentrations

The reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has $K_c = 4.06$ at 500 °C. If 0.100 mol of CO and 0.100 mol of $H_2O(g)$ are placed in a 1.00 liter reaction vessel at this temperature, what are the concentrations of the reactants and products when the system reaches equilibrium?

Analysis: The key to solving this kind of problem is recognizing that at equilibrium the mass action expression *must* equal K_c. We must find values for the concentrations that satisfy this condition. Although we aren't given any of the equilibrium values, we know that whatever they are, they are related to each other by the equilibrium law.

Assembling the Tools: Our tools in setting up the calculation will be the equilibrium law,

$$\frac{[CO_2][H_2]}{[CO][H_2O]} = 4.06 \qquad \text{(at equilibrium)}$$

and the concentration table. The problem gives us information about the initial concentrations, which we'll use to establish values for the first line of the table. If we knew how much the concentrations change, we could calculate the equilibrium concentrations. There are no data that let us calculate directly what any of the changes are, so we will represent them algebraically as unknowns. Combining the changes with the initial concentrations will give us algebraic expressions for the equilibrium concentrations. The relationship among the equilibrium concentrations is established by substituting them into the mass action expression.

The quantities representing the equilibrium concentrations must satisfy the equation given by the equilibrium law.

Solution: To build the table, we need quantities to enter into the "initial concentrations," "changes in concentrations," and "equilibrium concentrations" rows.

Initial Concentrations

The initial concentrations of CO and H_2O are each 0.100 mol/1.00 L = 0.100 *M*. Since no CO_2 or H_2 are initially placed into the reaction vessel, their initial concentrations both are zero. These are shown in red in the table.

Changes in Concentration

Some CO_2 and H_2 must form for the reaction to reach equilibrium. This also means that some CO and H_2O must react. But how much? If we knew the answer, we could calculate the equilibrium concentrations. Therefore, the changes in concentration are our unknown quantities.

Let us allow x to be equal to the number of moles per liter of CO that react. The change in the concentration of CO is then $-x$ (it is negative because the change decreases the CO concentration). Because CO and H_2O react in a 1:1 mole ratio, the change in the H_2O concentration is also $-x$. Since one mole each of CO_2 and H_2 are formed from one mole of CO, the CO_2 and H_2O concentrations each increase by x (their changes are $+x$). These quantities are shown in blue.

We could just as easily have chosen x to be the number of mol/L of H_2O that reacts or the number of mol/L of CO_2 or H_2 that forms. There's nothing special about having chosen CO to define x.

Equilibrium Concentrations

We obtain the equilibrium concentrations as

$$\begin{pmatrix}\text{equilibrium}\\ \text{concentration}\end{pmatrix} = \begin{pmatrix}\text{initial}\\ \text{concentration}\end{pmatrix} + \begin{pmatrix}\text{change in}\\ \text{concentration}\end{pmatrix}$$

Here is the completed concentration table.

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial concentrations (*M*)	0.100		0.100		0.0		0.0
Changes in concentrations (*M*)	$-x$		$-x$		$+x$		$+x$
Equilibrium concentrations (*M*)	$0.100 - x$		$0.100 - x$		x		x

We know that the quantities in the last row must satisfy the equilibrium law, so we substitute them into the mass action expression and solve for x.

$$\frac{(x)(x)}{(0.100 - x)(0.100 - x)} = 4.06$$

which we can write as

$$\frac{x^2}{(0.100 - x)^2} = 4.06$$

In this problem we can solve the equation for x most easily by taking the square root of both sides.

$$\sqrt{\frac{x^2}{(0.100 - x)^2}} = \frac{x}{(0.100 - x)} = \sqrt{4.06} = 2.01$$

Clearing fractions gives

$$x = 2.01(0.100 - x)$$
$$x = 0.201 - 2.01x$$

Collecting terms in x gives

$$x + 2.01x = 0.201$$
$$3.01x = 0.201$$
$$x = 0.0668$$

Now that we know the value of x, we can calculate the equilibrium concentrations from the last row of the table.

$$[CO] = 0.100 - x = 0.100 - 0.0668 = 0.033\ M$$
$$[H_2O] = 0.100 - x = 0.100 - 0.0668 = 0.033\ M$$
$$[CO_2] = x = 0.0668\ M$$
$$[H_2] = x = 0.0668\ M$$

■ **Is the Answer Reasonable?** First, we should check to see that all equilibrium concentrations are positive numbers (which they must be because a negative concentration is meaningless). They are. As in the preceding example, we can check the answer by substituting the equilibrium concentrations we've found into the mass action expression and evaluate the reaction quotient.

$$Q = \frac{(0.0668)^2}{(0.033)^2} = 4.1$$

Once again, Q is quite close to K_c, so we can be confident our answers are correct.

Example 15.9

Using K_c to Calculate Equilibrium Concentrations

In the preceding example (Example 15.8) it was stated that the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has $K_c = 4.06$ at 500 °C. Suppose 0.0600 mol each of CO and H_2O are mixed with 0.100 mol each of CO_2 and H_2 in a 1.00 L reaction vessel. What will the concentrations of all of the substances be when the mixture reaches equilibrium at this temperature?

■ **Analysis:** We will proceed in much the same way as in Example 15.8. However, this time determining the algebraic signs of x will not be quite so simple because none of the initial concentrations is zero. The best way to determine the algebraic signs is to use the initial concentrations to calculate the initial reaction quotient. We can then compare Q to K_c, and by reasoning, figure out which way the reaction must proceed to make Q equal to K_c.

Assembling the Tools: The equilibrium law for the reaction is

$$\frac{[CO_2][H_2]}{[CO][H_2O]} = K_c$$

One of our tools will be the mass action expression, from which we can calculate the initial value of Q. Once we know in which direction the reaction must proceed to reach equilibrium, we can construct the concentration table.

Solution: First we use the initial concentrations, shown in the first row of the concentration table below, to determine the initial value of the reaction quotient.

$$Q_{\text{initial}} = \frac{(0.100)(0.100)}{(0.0600)(0.0600)} = 2.78 < K_c$$

As indicated, Q_{initial} is less than K_c, so the system is not at equilibrium. To reach equilibrium Q must become larger, which requires an increase in the concentrations of CO_2 and H_2 as the reaction proceeds. This means that for CO_2 and H_2, the change must be positive, and, for CO and H_2O, the change must be negative.

Here is the completed concentration table.

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial concentrations (M)	0.0600		0.0600		0.100		0.100
Change in concentrations (M)	$-x$		$-x$		$+x$		$+x$
Equilibrium concentrations (M)	$0.0600 - x$		$0.0600 - x$		$0.100 + x$		$0.100 + x$

As before, we substitute equilibrium quantities into the mass action expression in the equilibrium law, which gives us

$$\frac{(0.100 + x)^2}{(0.0600 - x)^2} = 4.06$$

Taking the square root of both sides yields

$$\frac{0.100 + x}{0.0600 - x} = 2.01$$

To solve for x we first multiply each side by $(0.0600 - x)$ to obtain

$$0.100 + x = 2.01(0.0600 - x)$$
$$0.100 + x = 0.121 - 2.01x$$

Collecting terms in x on one side and the constants on the other gives

$$x + 2.01x = 0.121 - 0.100$$
$$3.01x = 0.021$$
$$x = 0.0070$$

Now we can calculate the equilibrium concentrations:

$$[CO] = [H_2O] = (0.0600 - x) = 0.0600 - 0.0070 = 0.0530\ M$$
$$[CO_2] = [H_2] = (0.100 + x) = 0.100 + 0.0070 = 0.107\ M$$

Is the Answer Reasonable? As a check, let's evaluate the reaction quotient using the calculated equilibrium concentrations.

$$Q = \frac{(0.107)^2}{(0.0530)^2} = 4.08$$

This is acceptably close to the value of K_c. (That it is not *exactly* equal to K_c is because of the rounding of answers during the calculations.)

In each of the preceding two examples, we were able to simplify the solution by taking the square root of both sides of the algebraic equation obtained by substituting equilibrium concentrations into the mass action expression. Such simplifications are not always possible, however, as illustrated in the next example.

Example 15.10
Using K_c to Calculate Equilibrium Concentrations

At a certain temperature, $K_c = 4.50$ for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If 0.300 mol of N_2O_4 is placed into a 2.00 L container at this temperature, what will be the equilibrium concentrations of both gases?

■ **Analysis:** As in Example 15.9, we will use the fact that at equilibrium the mass action expression must be equal to K_c. Because neither of the equilibrium concentrations are given, we will have to find algebraic expressions for the equilibrium concentrations and substitute them into the mass action expression.

■ **Assembling the Tools:** As usual, our principal tools will be the equilibrium law,

$$\frac{[NO_2]^2}{[N_2O_4]} = 4.50$$

and the concentration table for the reaction. We also have to use the definition of molarity to calculate the initial molar concentration of N_2O_4 from the data given in the problem.

■ **Solution:** The first step is constructing the concentration table.

Initial Concentrations

The initial concentration of N_2O_4 is 0.300 mol/2.00 L = 0.150 *M*. Since no NO_2 was placed in the reaction vessel, its initial concentration is 0.000 *M*.

■ Any time an initial concentration equals zero, we know it must change in a positive direction. It can't become less than zero.

Changes in Concentrations

There is no NO_2 in the reaction mixture, so we know its concentration must increase. This means the N_2O_4 concentration must decrease as some of the NO_2 is formed. Let's allow x to be the number of moles per liter of N_2O_4 that reacts, so the change in the N_2O_4 concentration is $-x$. Because of the stoichiometry of the reaction, the NO_2 concentration must increase by $2x$, so its change in concentration is $+2x$.

Equilibrium Concentrations

As before, we add the change to the initial concentration in each column to obtain expressions for the equilibrium concentrations.

■ In problems where the changes in concentrations are unknown, we can let the coefficients of *x* be the same as the coefficients in the balanced equation. This ensures they are in the correct ratio.

Here is the completed concentration table.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial concentrations (*M*)	0.150		0.000
Changes in concentrations (*M*)	$-x$		$+2x$
Equilibrium concentrations (*M*)	$0.150 - x$		$2x$

To obtain the solution, we substitute the equilibrium quantities into the mass action expression.

$$\frac{(2x)^2}{(0.150 - x)} = 4.50$$

or

$$\frac{4x^2}{(0.150 - x)} = 4.50 \tag{15.11}$$

This time the left side of the equation is not a perfect square, so we cannot just take the square root of both sides as in Examples 15.8 and 15.9. However, because the equation involves terms in x^2, x, and a constant, we can use the quadratic formula. Recall that for a quadratic equation of the form

$$ax^2 + bx + c = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Expanding Equation 15.11 gives

$$4x^2 = 4.50\,(0.150 - x)$$
$$4x^2 = 0.675 - 4.50x$$

Arranging terms in the standard order gives

$$4x^2 + 4.50x - 0.675 = 0$$

Therefore, the quantities we will substitute into the quadratic formula are as follows: $a = 4$, $b = 4.50$, and $c = -0.675$. Making these substitutions gives

$$\begin{aligned} x &= \frac{-4.50 \pm \sqrt{(4.50)^2 - 4(4)(-0.675)}}{2(4)} \\ &= \frac{-4.50 \pm \sqrt{31.05}}{8} \\ &= \frac{-4.50 \pm 5.57}{8} \end{aligned}$$

Because of the ± term, there are two values of x that satisfy the equation, $x = 0.134$ and $x = -1.26$. However, only the first value, $x = 0.134$, makes any sense chemically, as described below. Using $x = 0.134$, the equilibrium concentrations are

$$[N_2O_4] = 0.150 - 0.134 = 0.016\ M$$
$$[NO_2] = 2(0.134) = 0.268\ M$$

Notice that if we had used the negative root, −1.26, the equilibrium concentration of NO_2 would be negative. Negative concentrations are impossible, so $x = -1.26$ is not acceptable *for chemical reasons*. In general, whenever you use the quadratic equation in a chemical calculation, one root will be satisfactory and the other will lead to answers that are nonsense.

■ **Is the Answer Reasonable?** Once again, we can evaluate the reaction quotient using the calculated equilibrium values. When we do this, we obtain $Q = 4.49$, which is acceptably close to the value of K_c given.

Practice Exercises

15.20 | During an experiment, 0.200 mol of H_2 and 0.200 mol of I_2 were placed into a 1.00 liter vessel where the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

came to equilibrium. For this reaction, $K_c = 49.5$ at the temperature of the experiment. What were the equilibrium concentrations of H_2, I_2, and HI?

15.21 | In an experiment, 0.200 mol H_2 and 0.100 mol I_2 were placed in a 1.00 L vessel where the following equilibrium was established:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

For this reaction, $K_c = 49.5$ at the temperature of the experiment. What were the equilibrium concentrations of H_2, I_2, and HI?

Equilibrium problems can be much more complex than the ones we have just discussed. However, sometimes you can make assumptions that simplify the problem so that an approximate solution can be obtained, as described next.

Calculations when K_c Is Very Small

Many chemical reactions have equilibrium constants that are either very large or very small. For example, most weak acids have very small values for K_c. Therefore, only very tiny amounts of products form when these weak acids react with water.

When the K_c for a reaction is very small, the position of equilibrium lies far to the left, toward the reactants. Usually this permits us to simplify the calculations considerably, as shown in Example 15.11.

Example 15.11

Simplifying Equilibrium Calculations for Reactions with a Small K_c

Hydrogen, a potential fuel, is found in great abundance in water. Before the hydrogen can be used as a fuel, however, it must be separated from the oxygen; the water must be split into H_2 and O_2. One possibility is thermal decomposition, but this requires very high temperatures. Even at 1000 °C, $K_c = 7.3 \times 10^{-18}$ for the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

If at 1000 °C the H_2O concentration in a reaction vessel is set initially at 0.100 *M*, what will the H_2 concentration be when the reaction reaches equilibrium?

■ **Analysis:** As in earlier problems of this type, we can anticipate that we will have to solve an algebraic equation to obtain the equilibrium concentrations, none of which are given in the problem. We will follow that approach and see where it leads us.

■ **Assembling the Tools:** One tool we will definitely need is the equilibrium law:

$$\frac{[H_2]^2[O_2]}{[H_2O]^2} = 7.3 \times 10^{-18}$$

Another will be the concentration table.

■ **Solution:** The first step will be to construct the concentration table. The changes in concentrations are unknown and will be represented by expressions that contain the unknown quantity *x*.

Initial Concentrations

The initial concentration of H_2O is 0.100 *M*; those of H_2 and O_2 are both 0.0 *M*.

Changes in Concentrations

We know the changes must be in the same ratio as the coefficients in the balanced equation, so we place *x*'s in this row with coefficients equal to those in the chemical equation. Because there are no products present initially, their changes must be positive and the change for the water must be negative.

The complete concentration table is

	$2H_2O(g)$	$\rightleftharpoons$	$2H_2(g)$	+	$O_2(g)$
Initial concentrations (*M*)	0.100		0.0		0.0
Changes in concentrations (*M*)	$-2x$		$+2x$		$+x$
Equilibrium concentrations (*M*)	$0.100 - 2x$		$2x$		x

Next, we substitute the equilibrium quantities from the last row into the mass action expression.

$$\frac{(2x)^2 x}{(0.100 - 2x)^2} = 7.3 \times 10^{-18}$$

or

$$\frac{4x^3}{(0.100 - 2x)^2} = 7.3 \times 10^{-18}$$

■ $(2x)^2 x = (4x^2)x = 4x^3$

This is a *cubic equation* (one term involves x^3) and can be rather difficult to solve unless we can simplify it. In this instance we are able to simplify because the very small value of K_c tells us that hardly any of the H_2O will decompose. Whatever the actual value of *x*, we know *in advance* that it is going to be very small. This means that 2*x* will also be very small, so when this tiny value is subtracted from 0.100, the result will still be very, very close to 0.100. We will make the assumption, then, that the term in the denominator will be essentially unchanged from 0.100 by subtracting 2*x* from it; that is, we will assume that $0.100 - 2x \approx 0.100$.

■ Even before we solve the problem, we know that hardly any H_2 and O_2 will be formed, because K_c is so small.

This assumption greatly simplifies the math. We now have

$$\begin{aligned}\frac{4x^3}{(0.100 - 2x)^2} \approx \frac{4x^3}{(0.100)^2} &= 7.3 \times 10^{-18} \\ 4x^3 &= (0.0100)(7.3 \times 10^{-18}) = 7.3 \times 10^{-20} \\ x^3 &= 1.8 \times 10^{-20} \\ x &= \sqrt[3]{1.8 \times 10^{-20}} \\ &= 2.6 \times 10^{-7}\end{aligned}$$

Notice that the value of *x* that we've obtained is indeed very small. If we double it and subtract the answer from 0.100, we still get 0.100 when we round to the correct number of significant figures (the third decimal place).

$$\begin{aligned}0.100 - 2x = 0.100 - 2(2.6 \times 10^{-7}) &= 0.09999948 \\ &= 0.100 \qquad \text{(rounded correctly)}\end{aligned}$$

■ Always be sure to check your assumptions when solving a problem of this kind.

This check verifies that our assumption was valid. Finally, we have to obtain the H_2 concentration. Our table gives

$$[H_2] = 2x$$

Therefore,

$$[H_2] = 2(2.6 \times 10^{-7}) = 5.2 \times 10^{-7}\ M$$

Is the Answer Reasonable? The equilibrium constant is very small for this reaction (7.3×10^{-18}), so we expect the amount of product at equilibrium to be small as well. The very low concentration of H_2 seems reasonable. The value of x was positive, which means that there was a decrease in reactant concentrations and an increase in product concentrations as we would expect if only reactants were originally present. Finally, we can check the calculation by seeing if the reaction quotient is equal to the equilibrium constant:

$$Q = \frac{[H_2]^2[O_2]}{[H_2O]^2} = \frac{(5.2 \times 10^{-7})^2(2.6 \times 10^{-7})}{0.100^2} = 7.0 \times 10^{-18}$$

which differs from the original equilibrium constant only because the value of x was rounded off when we took the cube root.

Situations that Suggest Simplification of the Math Will Work

When the value of K_c or K_P is very small, the position of equilibrium lies far to the left, very near the reactants. This means that if we start with just reactants, the concentrations will hardly change. Under these conditions, the simplifying assumption made in Example 15.11 is valid because the small change in the reactant concentration, x, is subtracted from a much larger value. We could also have neglected x (or $2x$) if it were a very small number that was being added to a much larger one. Remember that you can only neglect an x that's *added* or *subtracted*; you can never drop an x that occurs as a multiplying or dividing factor. Some examples are

TOOLS

Simplifications in equilibrium calculations

$$x(0.100 - x)$$

You would never be justified in neglecting this x.

You are justified in neglecting this x, if x is small compared to 0.100.

$$\frac{(0.100 + x)}{x}$$

As a rule of thumb, you can expect that these simplifying assumptions will be valid if the concentration from which x is subtracted, or to which x is added, is at least 1000 times greater than K. For instance, in the preceding example, $2x$ was subtracted from 0.100. Since 0.100 is much larger than $1000 \times (7.3 \times 10^{-18})$ we expect the assumption $0.100 - 2x \approx 0.100$ to be valid. However, even though the simplifying assumption is *expected* to be valid, always check to see if it really is after finishing the calculation. If the assumption proves invalid, then some other way to solve the algebra must be found.

Practice Exercises

15.22 | At 25 °C, the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ has $K_c = 2.3 \times 10^{-9}$. If 0.041 mol NH_3 is placed in a 1.00 L container, what will the concentrations of N_2 and H_2 be when equilibrium is established? (*Hint:* Review the math below the concentration table in Example 15.11.)

15.23 | In air at 25 °C and 1.00 atm, the N_2 concentration is 0.033 M and the O_2 concentration is 0.00810 M. The reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

has $K_c = 4.8 \times 10^{-31}$ at 25 °C. Taking the N_2 and O_2 concentrations given above as initial values, calculate the equilibrium NO concentration that should exist in our atmosphere from this reaction at 25 °C.

Analyzing and Solving Multi-Concept Problems

The reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

has $K_P = 1.65 \times 10^{11}$ at 25 °C. Suppose a mixture of the reactants is prepared at 25 °C by transferring 1.15 g of NO and 645 mL of O_2 measured at 33 °C and 800 torr into a 1.00 L vessel. When the mixture comes to equilibrium, what will be the concentrations of each of the three gases?

Analysis As with all equilibrium problems, we are going to work with the equilibrium law. For this gaseous reaction, we can write this as

$$\frac{[NO_2]^2}{[NO]^2[O_2]} = K_c \qquad \text{or} \qquad \frac{P^2_{NO_2}}{P^2_{NO}P_{O_2}} = K_P$$

We've been given K_P, but we know we can convert this to K_c. This was covered in Section 15.3. (Although we could work with K_P, this problem will be easier if we use K_c instead, because we're looking for equilibrium concentrations.)

Before we can construct the concentration table, we need the initial concentrations of the reactants. For NO, we have to convert grams to moles, which you learned to do in Chapter 4. For O_2, we must use the *P, V, T* data to find moles of O_2.

Assembling the Tools To find K_c, we have to use Equation 15.9, $K_P = K_c(RT)^{\Delta n_g}$. Solving for K_c gives

$$K_c = \frac{K_P}{(RT)^{\Delta n_g}} = K_P(RT)^{-\Delta n_g} \qquad \textbf{(15.12)}$$

Remember that $R = 0.0821$ L atm mol^{-1} K^{-1} and T is the Kelvin temperature.

To calculate the moles of NO placed in the reaction vessel, our tool is the molar mass of NO, which is 30.01 g mol^{-1}. To find moles of O_2, the tool is the ideal gas law, which we solve for n_{O_2},

$$n_{O_2} = \frac{PV}{RT}$$

The definition of molarity provides the tool to calculate the molarity of each reactant.

Solution First we calculate K_c. Taking coefficients to represent moles, the reaction has two moles of gaseous products and three moles of gaseous reactants. Therefore, $\Delta n_g = -1$. Substituting values into Equation 15.12 gives

$$K_c = 1.65 \times 10^{11}\ [(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})]^{-(-1)}$$
$$= 4.04 \times 10^{12}$$

Next, we calculate initial moles of each reactant.

Moles of NO

$$1.15 \text{ g NO} \times \frac{1 \text{ mol NO}}{30.01 \text{ g NO}} = 0.0383 \text{ mol NO}$$

Moles of O_2

$$n_{O_2} = \frac{PV}{RT} = \frac{\left(\frac{800 \text{ torr}}{760 \text{ torr/atm}}\right) \times 0.645 \text{ L}}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})}$$
$$= 0.0278 \text{ mol } O_2$$

Both reactants are in the 1.00 L vessel, so their initial concentrations are [NO] = 0.0383 *M* and $[O_2]$ = 0.0278 *M*. No NO_2 was placed in the vessel, so its initial concentration is zero. Here's the concentration table, assembled in the usual way.

	$2NO(g)$	$+\ O_2(g)$	$\rightleftharpoons\ 2NO_2(g)$
Initial concentrations (*M*)	0.0383	0.0278	0.000
Changes in concentrations (*M*)	$-2x$	$-x$	$+2x$
Equilibrium concentrations (*M*)	$0.0383 - 2x$	$0.0278 - x$	$2x$

Substituting equilibrium quantities into the equilibrium law gives

$$K_c = 4.04 \times 10^{12} = \frac{(2x)^2}{(0.0383 - 2x)^2(0.0278 - x)}$$

We might be tempted to assume that x (or $2x$) is negligibly small and can be dropped, which would make the algebra manageable. However, this isn't going to work here. The very large value of K_c tells us this reaction proceeds far toward completion, so almost all of at least one of the reactants will be consumed. *This means the changes in concentration are not small and can't be ignored.* So, the question is, can we reshape the problem to make it possible to solve it?

■ If you drop $2x$ and x in the terms in the denominator and then solve for x, you get $x = 6.4 \times 10^3$, a number that is certainly not small compared with 0.0383 or 0.0278.

Recasting the Problem

Analysis The algebra will be manageable if we can start the calculation with the system very close to equilibrium. In this reaction the position of equilibrium lies far to the right, as indicated by the value of K_c. Because the same equilibrium concentrations are reached regardless of whether we approach equilibrium from the left or the right, we are going to assume equilibrium in this system is reached in two steps. Step 1 will involve the complete reaction of the initial NO and O_2 to give NO_2. This is actually a limiting reactant problem. Step 2 will involve approaching equilibrium from the right. This will require that we rework the concentration table starting from the product side.

STEP 1

Assembling the Tools The tool is the method of working limiting reactant problems, which you learned in Chapter 4.

Solution We start with 0.0383 mol NO and 0.0278 mol O_2. If all the NO were to react, it would require only 0.0192 mol O_2,

$$0.0383 \text{ mol NO} \times \frac{1 \text{ mol } O_2}{2 \text{ mol NO}} = 0.0192 \text{ mol } O_2$$

Therefore, O_2 is in excess and NO is limiting. Based on the coefficients in the equation, if all the NO reacts, it will form 0.0383 mol NO_2 and the amount of O_2 remaining will be (0.0278 mol − 0.0192 mol) = 0.0086 mol.

STEP 2

Assembling the Tools The tools will be the same as those we tried initially when we attempted to solve the problem.

Solution Here are our new initial starting conditions:

$$[NO] = 0.000\ M \qquad \text{(We've assumed all initially present reacted.)}$$
$$[O_2] = 0.0086\ M$$
$$[NO_2] = 0.0383\ M$$

The new concentration table is shown below. Notice that the signs have changed for the "changes in concentration" row. This reflects that we are now starting at the product side and that the reaction that's occurring is the one from right to left.

	$2NO(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2NO_2(g)$
Initial concentrations (*M*)	0.000	0.0086	0.0383
Changes in concentrations (*M*)	$+2x$	$+x$	$-2x$
Equilibrium concentrations (*M*)	$2x$	$0.0086 + x$	$0.0383 - 2x$

Substituting values from the last row into the mass action expression gives

$$K_c = 4.04 \times 10^{12} = \frac{(0.0383 - 2x)^2}{(2x)^2(0.0086 + x)}$$

We know that, by starting at the product side, we are very close to equilibrium and therefore x and $2x$ are going to be small compared to the initial concentrations, so we feel safe in neglecting them. This gives

$$K_c = 4.04 \times 10^{12} \approx \frac{(0.0383)^2}{(4x^2)(0.0086)}$$

This can be solved for x to give $x = 1.03 \times 10^{-7}$. Using the quantities in the last row of the concentration table above, the equilibrium concentrations are as follows:

$$[NO] = 2 \times (1.03 \times 10^{-7}) = 2.06 \times 10^{-7}\ M$$
$$[O_2] = (0.0086 + 1.03 \times 10^{-7}) = 0.0086\ M \quad \text{(correctly rounded)}$$
$$[NO_2] = [0.0383 - 2 \times (1.03 \times 10^{-7})] = 0.0383\ M \quad \text{(correctly rounded)}$$

Are the Answers Reasonable? First, notice that after recasting the problem, we are justified in making the simplifying assumptions that made the mathematical equation easily solvable. We can also check the answers by substituting them into the mass action expression.

$$Q = \frac{(0.0383)^2}{(2.06 \times 10^{-7})^2(0.0086)} = 4.02 \times 10^{12} = K_c$$

The answers we've obtained satisfy the equilibrium law, so we can be confident they are correct.

Summary

Dynamic Equilibrium. When the forward and reverse reactions in a chemical system occur at equal rates, a dynamic equilibrium exists and the concentrations of the reactants and products remain constant. For a given overall chemical composition, the amounts of reactants and products that are present at equilibrium are the same regardless of whether the equilibrium is approached from the direction of pure “reactants,” pure “products,” or any mixture of them. (In a chemical equilibrium, the terms *reactants* and *products* do not have the usual significance because the reaction is proceeding in both directions simultaneously. Instead, we use *reactants* and *products* simply to identify the substances on the left- and right-hand sides, respectively, of the equation for the equilibrium.)

The Equilibrium Law. The **mass action expression** is a fraction. The concentrations of the products, raised to powers equal to their coefficients in the chemical equation for a **homogeneous equilibrium**, are multiplied together in the numerator. The denominator is constructed in the same way from the concentrations of the reactants raised to powers equal to their coefficients. The numerical value of the mass action expression is the **reaction quotient, Q**. At equilibrium, the reaction quotient is equal to the **equilibrium constant, K_c**. If partial pressures of gases are used in the mass action expression, **K_P** is obtained. The magnitude of the equilibrium constant is roughly proportional to the extent to which the reaction proceeds to completion when equilibrium is reached. Equilibrium equations can be manipulated by multiplying the coefficients by a common factor, changing the direction of the reaction, and by adding two or more equilibria. The rules given in the description of the *Tools for Problem Solving* below apply.

Relating K_P to K_c. The values of K_P and K_c are only equal if the same number of moles of gas are represented on both sides of the chemical equation. When the number of moles of gas are different, K_P is related to K_c by the equation $K_P = K_c(RT)^{\Delta n_g}$. Remember to use $R = 0.0821$ L atm mol^{-1} K^{-1} and T = absolute temperature. Also, be careful to calculate Δn_g as the difference between the number of moles of *gaseous* products and the number of moles of *gaseous* reactants in the balanced equation.

Heterogeneous Equilibria. An equilibrium involving substances in more than one phase is a **heterogeneous equilibrium**. The mass action expression for a heterogeneous equilibrium omits concentration terms for pure liquids and/or pure solids.

Le Châtelier’s Principle. This principle states that *when an equilibrium is upset by some disturbance, a chemical change occurs in a direction that opposes the disturbing influence and brings the system to equilibrium again.* Adding a reactant or a product causes a reaction to occur that uses up part of what has been added. Removing a reactant or a product causes a reaction that replaces part of what has been removed. Increasing the pressure (by reducing the volume) drives a reaction in the direction of the fewer number of moles of gas. Altering the pressure on an equilibrium system involving only solids and liquids has virtually no effect on the position of equilibrium. Raising the temperature causes an equilibrium to shift in an endothermic direction. The value of K increases with increasing temperature for reactions that are endothermic in the forward direction. A change in temperature is the only factor that changes K. Addition of a catalyst or an inert gas has no effect on an equilibrium.

Equilibrium Calculations. The initial concentrations in a chemical system are controlled by the person who combines the chemicals at the start of the reaction. The changes in concentration are determined by the stoichiometry of the reaction. Only equilibrium concentrations satisfy the equilibrium law. When these are used, the value of the mass action expression, Q, is equal to K_c. When a change in concentration is expected to be very small compared to the initial concentration, the change may be neglected and the algebraic equation derived from the equilibrium law can be simplified. In general, this simplification is valid if the initial concentration is at least 1000 times larger than K.

TOOLS

Tools for Problem Solving The following tools related to solving chemical equilibria problems were introduced in this chapter.

The approach to equilibrium (page 698)

There are times (such as in *Analyzing and Solving Multi-Concept Problems,* page 729) when it is very helpful to remember that the same equilibrium composition is reached regardless of whether it is approached from the reactants or from the products. When K_c or K_P is very large, equilibrium problems can be greatly simplified if we first imagine the reaction going to completion (converting all the reactants to products) and then approaching the equilibrium from the direction of the products.

Requirement for equilibrium (page 700)

For a system to be at equilibrium, the numerical value of Q must equal the equilibrium constant. Use this tool to determine whether a system is at equilibrium when you have a way to calculate Q. By comparing Q with K, you can determine the direction the reaction must proceed to reach equilibrium.

The equilibrium law (page 701)

To solve most chemical equilibrium problems we need the equation for the equilibrium and the equilibrium law. Knowing how to construct the equilibrium law from the chemical equation is an essential tool for dealing with such problems. For a homogeneous reaction, an equation of the form

$$dD + eE \rightleftharpoons fF + gG$$

has the equilibrium law

$$\frac{[F]^f[G]^g}{[D]^d[E]^e} = K_c$$

Remember that for gaseous reactions, partial pressures can be used in place of concentrations, in which case the mass action expression equals K_P. In general, K_P does not equal K_c.

Manipulating equilibrium equations (pages 702 and 703)

There are occasions when it is necessary to modify an equation for an equilibrium, or to combine two or more chemical equilibria. The tools discussed here are used to obtain the new equilibrium constants for the new equations.

- When two equations are added, we multiply their *K*s to obtain the new *K*.
- When an equation is multiplied by a factor *n* to obtain a new equation, we raise its *K* to the power *n* to obtain the *K* for the new equation.
- When an equation is reversed, we take the reciprocal of its *K* to obtain the new *K*.

Converting between K_P and K_c (page 705)

To relate K_P to K_c, we use the equation

$$K_P = K_c(RT)^{\Delta n_g}$$

Remember to use $R = 0.0821$ L atm mol^{-1} K^{-1}. Also, remember that Δn_g is the change in moles of gas on going from reactants to products. In Chapter 19 you will learn how to calculate equilibrium constants from thermodynamic data. These calculations give K_P for gaseous reactions.

Equilibrium laws for heterogeneous reactions (page 707)

Being able to write the equilibrium law for a heterogeneous reaction is a tool you will need in later chapters when we deal with solubility equilibria. Remember that pure solids and pure liquids do not appear in the mass action expression.

Significance of the magnitude of *K* (page 709)

Use this tool to make a rough estimate of the position of equilibrium.

- When *K* is very large, the position of equilibrium lies far to the right (toward the products).
- When *K* is very small, the position of equilibrium lies far to the left (toward the reactants).

Le Châtelier's principle

This tool lets us predict how disturbing influences shift the position of equilibrium. Factors to consider are:

- Adding or removing a reactant or product (page 711)
- Changing the volume of a gaseous equilibrium (page 712)
- Raising or lowering the temperature (page 713)
- Changing temperature changes *K* (page 714)

Catalysts or inert gases have no effect on the position of equilibrium.

Concentration table (page 716)

This is a tool you will use in almost all equilibrium calculations. Remember the following points when constructing the table:

- All entries in the table must have units of molarity (mol L^{-1}).
- Any reactant or product for which an initial concentration or amount is not given in the statement of the problem is assigned an initial concentration of zero.
- Any substance with an initial concentration of zero *must* have a positive change in concentration when the reaction proceeds to equilibrium.
- The changes in concentration are in the same ratio as the coefficients in the balanced equation. When the changes are unknown, the coefficients of *x* can be the same as the coefficients in the balanced equation.
- Only quantities in the last row (equilibrium concentrations) satisfy the equilibrium law.

Simplifications in equilibrium calculations (page 728)

When the initial reactant concentrations are larger than 1000 × K, they will change only slightly as the reaction approaches equilibrium. You can therefore expect to be able to neglect the change when it is being added to or subtracted from an initial concentration. This tool is especially useful when working problems in which K is very small and the initial conditions are not far from the final position of equilibrium. *If you use simplifying approximations, be sure to check their validity after obtaining an answer.*

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

General

15.1 Sketch a graph showing how the concentrations of the reactants and products of a typical chemical reaction vary with time during the course of the reaction. Assume no products are present at the start of the reaction. Indicate on the graph where the system has reached equilibrium.

15.2 What meanings do the terms *reactants* and *products* have when describing a chemical equilibrium?

Mass Action Expression, K_P and K_c

15.3 What is an *equilibrium law*? How is the term *reaction quotient* defined? What symbol is it given?

15.4 Under what conditions does the reaction quotient equal K_c?

15.5 Suppose for the reaction $A \rightarrow B$ the value of Q is less than K_c. Which way does the reaction have to proceed to reach equilibrium—in the forward or reverse direction?

15.6 When a chemical equation and its equilibrium constant are given, why is it not necessary to also specify the form of the mass action expression?

15.7 At 225 °C, $K_P = 6.3 \times 10^{-3}$ for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Would we expect this reaction to go nearly to completion?

15.8 Here are some reactions and their equilibrium constants.

(a) $2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \quad K_c = 9.5 \times 10^{-13}$

(b) $CH_3OH(g) + H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad K_c = 3.6 \times 10^{20}$

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad K_c = 2.0 \times 10^{9}$

Arrange these reactions in order of their increasing tendency to go to completion.

Converting between K_P and K_c

15.9 State the equation relating K_P to K_c and define all terms. Which is the only value of R that can be properly used in this equation?

15.10 Use the ideal gas law to show that the partial pressure of a gas is directly proportional to its molar concentration. What is the proportionality constant?

Heterogeneous Equilibria

15.11 What is the difference between a *heterogeneous equilibrium* and a *homogeneous equilibrium*?

15.12 Why do we omit the concentrations of pure liquids and pure solids from the mass action expression of heterogeneous reactions?

15.13 Consider the following equilibrium.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

If you were converting between K_P and K_c, what value of Δn_g would you use?

Le Châtelier's Principle

15.14 State Le Châtelier's principle in your own words.

15.15 Explain, using its effect on the reaction quotient, why adding a reactant to the following equilibrium shifts the position of equilibrium to the right.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

15.16 Halving the volume of a gas doubles its pressure. Using the reaction quotient corresponding to K_P, explain why halving the volume shifts the following equilibrium to the left.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

15.17 How will the value of K_P for the following reactions be affected by an increase in temperature?

(a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H^\circ = -18\ \text{kJ}$

(b) $N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g) \quad \Delta H^\circ = +155.7\ \text{kJ}$

(c) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \quad \Delta H^\circ = -77.07\ \text{kJ}$

15.18 Why doesn't a catalyst affect the position of equilibrium in a chemical reaction?

Review Problems

Equilibrium Laws for K_P and K_c

15.19 Write the equilibrium law for each of the following gaseous reactions in terms of molar concentrations:

(a) $2PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(c) $N_2H_4(g) + 2O_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$

(d) $N_2H_4(g) + 6H_2O_2(g) \rightleftharpoons 2NO_2(g) + 8H_2O(g)$

(e) $SOCl_2(g) + H_2O(g) \rightleftharpoons SO_2(g) + 2HCl(g)$

15.20 Write the equilibrium law for each of the following gaseous reactions in terms of molar concentrations.

(a) $3Cl_2(g) + NH_3(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$

(b) $PCl_3(g) + PBr_3(g) \rightleftharpoons PCl_2Br(g) + PClBr_2(g)$

(c) $NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_2(g)$

(d) $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$

(e) $Br_2(g) + 5F_2(g) \rightleftharpoons 2BrF_5(g)$

15.21 Write the equilibrium law for the reactions in Problem 15.19 in terms of partial pressures.

15.22 Write the equilibrium law for the reactions in Problem 15.20 in terms of partial pressures.

OH **15.23** Write the equilibrium law for each of the following reactions in aqueous solution.

(a) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

(b) $Cd^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons Cd(SCN)_4{}^{2-}(aq)$

15.24 Write the equilibrium law for each of the following reactions in aqueous solution.

(a) $HClO(aq) + H_2O \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

(b) $CO_3{}^{2-}(aq) + HSO_4{}^-(aq) \rightleftharpoons HCO_3{}^-(aq) + SO_4{}^{2-}(aq)$

Manipulating Equilibrium Equations

15.25 At 25 °C, $K_c = 1 \times 10^{-85}$ for the reaction

$$7IO_3{}^-(aq) + 9H_2O + 7H^+(aq) \rightleftharpoons I_2(aq) + 5H_5IO_6(aq)$$

What is the value of K_c for the following reaction?

$$I_2(aq) + 5H_5IO_6(aq) \rightleftharpoons 7IO_3{}^-(aq) + 9H_2O + 7H^+(aq)$$

15.26 Use the following equilibria

$$2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \qquad K_c = 9.5 \times 10^{-13}$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + H_2(g) \qquad K_c = 2.8 \times 10^{-21}$$

to calculate K_c for the reaction

$$2CH_3OH(g) + H_2(g) \rightleftharpoons C_2H_6(g) + 2H_2O(g)$$

15.27 Write the equilibrium law for each of the following reactions in terms of molar concentrations:

(a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$

How does K_c for reaction (a) compare with K_c for reaction (b)?

15.28 Write the equilibrium law for the reaction

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

How does K_c for this reaction compare with K_c for reaction (a) in Problem 15.27?

Converting between K_P and K_c

15.29 A 345 mL container holds NH_3 at a pressure of 745 torr and a temperature of 45 °C. What is the molar concentration of ammonia in the container?

15.30 In a certain container at 145 °C the concentration of water vapor is 0.0200 *M*. What is the partial pressure of H_2O in the container?

15.31 For which of the following reactions does $K_P = K_c$?

(a) $2H_2(g) + C_2H_2(g) \rightleftharpoons C_2H_6(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

OH **15.32** For which of the following reactions does $K_P = K_c$?

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(b) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

OH ILW **15.33** The reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $K_P = 6.3 \times 10^{-3}$ at 225 °C. What is the value of K_c at this temperature?

15.34 The reaction $HCO_2H(g) \rightleftharpoons CO(g) + H_2O(g)$ has $K_P = 1.6 \times 10^6$ at 400 °C. What is the value of K_c for this reaction at this temperature?

15.35 The reaction $N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$ has $K_c = 4.2 \times 10^{-4}$ at 500 °C. What is the value of K_P at this temperature?

15.36 One possible way of removing NO from the exhaust of a gasoline engine is to cause it to react with CO in the presence of a suitable catalyst.

$$2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$$

At 300 °C, this reaction has $K_c = 2.2 \times 10^{59}$. What is K_P at 300 °C?

15.37 At 773 °C the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $K_c = 0.40$. What is K_P at this temperature?

15.38 The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has $K_P = 4.6 \times 10^{-2}$ at 395 °C. What is K_c at this temperature?

Heterogeneous Equilibria

15.39 Calculate the molar concentration of water in **(a)** 18.0 mL of $H_2O(l)$, **(b)** 100.0 mL of $H_2O(l)$, and **(c)** 1.00 L of $H_2O(l)$. Assume that the density of water is 1.00 g/mL.

15.40 The density of sodium chloride is 2.164 g cm^{-3}. What is the molar concentration of NaCl in a 12.0 cm^3 sample of pure NaCl? What is the molar concentration of NaCl in a 25.0 g sample of pure NaCl?

15.41 Write the equilibrium law corresponding to K_c for each of the following heterogeneous reactions.

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

(b) $2NaHSO_3(s) \rightleftharpoons Na_2SO_3(s) + H_2O(g) + SO_2(g)$

(c) $2C(s) + 2H_2O(g) \rightleftharpoons CH_4(g) + CO_2(g)$

(d) $CaCO_3(s) + 2HF(g) \rightleftharpoons CaF_2(s) + H_2O(g) + CO_2(g)$

(e) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

15.42 Write the equilibrium law corresponding to K_c for each of the following heterogeneous reactions.

(a) $CaCO_3(s) + SO_2(g) \rightleftharpoons CaSO_3(s) + CO_2(g)$

(b) $AgCl(s) + Br^-(aq) \rightleftharpoons AgBr(s) + Cl^-(aq)$

(c) $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

(d) $Mg(OH)_2(s) \rightleftharpoons MgO(s) + H_2O(g)$

(e) $3CuO(s) + 2NH_3(g) \rightleftharpoons 3Cu(s) + N_2(g) + 3H_2O(g)$

OH **15.43** The heterogeneous reaction $2HCl(g) + I_2(s) \rightleftharpoons 2HI(g) + Cl_2(g)$ has $K_c = 1.6 \times 10^{-34}$ at 25 °C. Suppose 0.100 mol of HCl and solid I_2 are placed in a 1.00 L container. What will be the equilibrium concentrations of HI and Cl_2 in the container?

15.44 At 25 °C, $K_c = 360$ for the reaction

$$AgCl(s) + Br^-(aq) \rightleftharpoons AgBr(s) + Cl^-(aq)$$

If solid AgCl is added to a solution containing 0.10 M Br^-, what will be the equilibrium concentrations of Br^- and Cl^-?

Le Châtelier's Principle

15.45 How will the position of equilibrium in the reaction

$$\text{heat} + CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

be affected by the following changes?

(a) Adding $CH_4(g)$

(b) Adding $H_2(g)$

(c) Removing $CS_2(g)$

(d) Decreasing in the volume of the container

(e) Increasing the temperature

OH **15.46** The reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $\Delta H° = -18$ kJ. How will the amount of CH_3OH present at equilibrium be affected by the following changes?

(a) Adding $CO(g)$

(b) Removing $H_2(g)$

(c) Decreasing the volume of the container

(d) Adding a catalyst

(e) Increasing the temperature

15.47 Consider the equilibrium

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g) \quad \Delta H° = +155.7 \text{ kJ}$$

In which direction will this equilibrium be shifted by the following changes?

(a) Adding N_2O

(b) Removing NO_2

(c) Adding NO

(d) Increasing the temperature of the reaction mixture

(e) Adding helium gas to the reaction mixture at constant volume

(f) Decreasing the volume of the container at constant temperature

15.48 Consider the equilibrium $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ for which $\Delta H° = -77.07$ kJ. How will the amount of Cl_2 at equilibrium be affected by the following changes?

(a) Removing $NO(g)$

(b) Adding $NOCl(g)$

(c) Raising the temperature

(d) Decreasing the volume of the container

Equilibrium Calculations

15.49 At a certain temperature, $K_c = 0.18$ for the equilibrium

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Suppose a reaction vessel at this temperature contained these three gases at the following concentrations: $[PCl_3] = 0.0420\ M$, $[Cl_2] = 0.0240\ M$, $[PCl_5] = 0.00500\ M$.

(a) Compute the reaction quotient and use it to determine whether the system is in a state of equilibrium.

(b) If the system is not at equilibrium, in which direction will the reaction proceed to get to equilibrium?

15.50 At 460 °C, the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has $K_c = 85.0$. A reaction flask at 460 °C contains these gases at the following concentrations: $[SO_2] = 0.00250\ M$, $[NO_2] = 0.00350\ M$, $[NO] = 0.0250\ M$, $[SO_3] = 0.0400\ M$.

(a) Is the reaction at equilibrium?

(b) If not, in which direction will the reaction proceed to arrive at equilibrium?

OH **15.51** At a certain temperature, the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

has $K_c = 0.500$. If a reaction mixture at equilibrium contains 0.180 M CO and 0.220 M H_2, what is the concentration of $CH_3OH(g)$?

15.52 $K_P = 0.018$ for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at a certain temperature. Suppose it was found that in an equilibrium mixture of these gases the partial pressure of $NH_3(g)$ is 22.2 atm and the partial pressure of N_2 is 1.18 atm. What is the partial pressure of $H_2(g)$?

15.53 At 773 °C, a mixture of $CO(g)$, $H_2(g)$, and $CH_3OH(g)$ was allowed to come to equilibrium. The following equilibrium concentrations were then measured: $[CO] = 0.105\ M$, $[H_2] = 0.250\ M$, $[CH_3OH] = 0.00261\ M$. Calculate K_c for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

15.54 Ethylene, C_2H_4, and water react under appropriate conditions to give ethanol. The reaction is

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

An equilibrium mixture of these gases at a certain temperature had the following partial pressures: $P_{C_2H_4} = 0.575$ atm, $P_{H_2O} = 1.30$ atm, $P_{C_2H_5OH} = 6.99$ atm. What is the value of K_P?

ILW **15.55** At high temperature, 2.00 mol of HBr was placed in a 4.00 L container where it decomposed to give the equilibrium

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

At equilibrium the concentration of Br_2 was measured to be $0.0955\ M$. What is K_c for this reaction at this temperature?

15.56 A 0.050 mol sample of formaldehyde vapor, CH_2O, was placed in a heated 500 mL vessel and some of it decomposed. The reaction is

$$CH_2O(g) \rightleftharpoons H_2(g) + CO(g)$$

At equilibrium, the $CH_2O(g)$ concentration was $0.066\ \text{mol L}^{-1}$. Calculate the value of K_c for this reaction.

15.57 The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ reached equilibrium at a certain high temperature. Originally, the reaction vessel contained the following initial concentrations: $[N_2O] = 0.184\ M$, $[O_2] = 0.377\ M$, $[NO_2] = 0.0560\ M$, and $[NO] = 0.294\ M$. The concentration of the NO_2, the only colored gas in the mixture, was monitored by following the intensity of the color. At equilibrium, the NO_2 concentration had become $0.118\ M$. What is the value of K_c for this reaction at this temperature?

15.58 At 25 °C, 0.0560 mol O_2 and 0.020 mol N_2O were placed in a 1.00 L container where the following equilibrium was then established.

$$2N_2O(g) + 3O_2(g) \rightleftharpoons 4NO_2(g)$$

At equilibrium, the NO_2 concentration was $0.020\ M$. What is the value of K_c for this reaction?

15.59 At 25 °C, $K_c = 0.145$ for the following reaction in the solvent CCl_4.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

If the initial concentration of BrCl in the solution is $0.050\ M$, what will the equilibrium concentrations of Br_2 and Cl_2 be?

15.60 At 25 °C, $K_c = 0.145$ for the following reaction in the solvent CCl_4.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

If the initial concentrations of Br_2 and Cl_2 are each $0.0250\ M$, what will their equilibrium concentrations be?

15.61 The equilibrium constant, K_c, for the reaction

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

was found to be 0.500 at a certain temperature. If 0.240 mol of SO_3 and 0.240 mol of NO are placed in a 2.00 L container and allowed to react, what will be the equilibrium concentration of each gas?

15.62 For the reaction in Problem 15.61, a reaction mixture is prepared in which 0.120 mol NO_2 and 0.120 mol of SO_2 are placed in a 1.00 L vessel. After the system reaches equilibrium, what will be the equilibrium concentrations of all four gases? How do these equilibrium values compare to those calculated in Problem 15.61? Account for your observation.

15.63 At a certain temperature the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has $K_c = 0.400$. Exactly 1.00 mol of each gas was placed in a 100.0 L vessel and the mixture underwent reaction. What was the equilibrium concentration of each gas?

15.64 At 25 °C, $K_c = 0.145$ for the following reaction in the solvent CCl_4.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

If the initial concentrations of each substance in a solution are $0.0400\ M$, what will their equilibrium concentrations be?

ILW **15.65** The reaction $2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$ has $K_c = 3.2 \times 10^{-34}$ at 25 °C. If a reaction vessel contains initially $0.0500\ \text{mol L}^{-1}$ of HCl and then reacts to reach equilibrium, what will be the concentrations of H_2 and Cl_2?

15.66 At 200 °C, $K_c = 1.4 \times 10^{-10}$ for the reaction

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$$

If 0.200 mol of N_2O and 0.400 mol NO_2 are placed in a 4.00 L container, what would the NO concentration be if this equilibrium were established?

ILW **15.67** At 2000 °C, the decomposition of CO_2,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

has $K_c = 6.4 \times 10^{-7}$. If a 1.00 L container holding 1.00×10^{-2} mol of CO_2 is heated to 2000 °C, what will be the concentration of CO at equilibrium?

15.68 At 500 °C, the decomposition of water into hydrogen and oxygen,

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

has $K_c = 6.0 \times 10^{-28}$. How many moles of H_2 and O_2 are present at equilibrium in a 5.00 L reaction vessel at this temperature if the container originally held 0.015 mol H_2O?

15.69 At a certain temperature, $K_c = 0.18$ for the equilibrium

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

If 0.026 mol of PCl_5 is placed in a 2.00 L vessel at this temperature, what will the concentration of PCl_3 be at equilibrium?

15.70 At 460 °C, the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has $K_c = 85.0$. Suppose 0.100 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO, and 0.120 mol of SO_3 are placed in a 10.0 L container at this temperature. What will the concentrations of all the gases be when the system reaches equilibrium?

15.71 At a certain temperature, $K_c = 0.500$ for the reaction

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

If 0.100 mol SO_3 and 0.200 mol NO are placed in a 2.00 L container and allowed to come to equilibrium, what will the NO_2 and SO_2 concentrations be?

15.72 At 25 °C, $K_c = 0.145$ for the following reaction in the solvent CCl_4.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

A solution was prepared with the following initial concentrations: [BrCl] = 0.0400 *M*, $[Br_2] = 0.0300$ *M*, and $[Cl_2] = 0.0200$ *M*. What will their equilibrium concentrations be?

***15.73** At a certain temperature, $K_c = 4.3 \times 10^5$ for the reaction

$$HCO_2H(g) \rightleftharpoons CO(g) + H_2O(g)$$

If 0.200 mol of HCO_2H is placed in a 1.00 L vessel, what will be the concentrations of CO and H_2O when the system reaches equilibrium? (*Hint:* Where does the position of equilibrium lie when *K* is very large?)

***15.74** The reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ has $K_c = 2.0 \times 10^9$ at 25 °C. If 0.100 mol of H_2 and 0.200 mol of Br_2 are placed in a 10.0 L container, what will all the equilibrium concentrations be at 25 °C? (*Hint:* Where does the position of equilibrium lie when *K* is very large?)

Additional Exercises

OH **15.75** The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ has $K_P = 0.140$ at 25 °C. In a reaction vessel containing these gases in equilibrium at this temperature, the partial pressure of N_2O_4 was 0.250 atm.

(a) What was the partial pressure of the NO_2 in the reaction mixture?

(b) What was the total pressure of the mixture of gases?

15.76 At 25 °C, the following concentrations were found for the gases in an equilibrium mixture for the reaction

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$$

$[NO_2] = 0.24$ *M*, $[NO] = 4.8 \times 10^{-8}$ *M*, and $[N_2O] = 0.023$ *M*. What is the value of K_P for this reaction?

15.77 The following reaction in aqueous solution has $K_c = 1 \times 10^{-85}$ at a temperature of 25 °C.

$$7IO_3^-(aq) + 9H_2O + 7H^+(aq) \rightleftharpoons I_2(aq) + 5H_5IO_6(aq)$$

What is the equilibrium law for this reaction?

***15.78** At a certain temperature, $K_c = 0.914$ for the reaction

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

A mixture was prepared containing 0.200 mol NO_2, 0.300 mol NO, 0.150 mol N_2O, and 0.250 mol O_2 in a 4.00 L container. What will be the equilibrium concentrations of each gas?

***15.79** At 27 °C, $K_P = 1.5 \times 10^{18}$ for the reaction

$$3NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

If 0.030 mol of NO were placed in a 1.00 L vessel and this equilibrium were established, what would be the equilibrium concentrations of NO, N_2O, and NO_2?

15.80 Consider the equilibrium

$$2NaHSO_3(s) \rightleftharpoons Na_2SO_3(s) + H_2O(g) + SO_2(g)$$

How will the position of equilibrium be affected by the following changes?

(a) Adding $NaHSO_3$ to the reaction vessel

(b) Removing Na_2SO_3 from the reaction vessel

(c) Adding H_2O to the reaction vessel

(d) Increasing the volume of the reaction vessel

15.81 At a certain temperature, $K_c = 0.914$ for the reaction

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

A mixture was prepared containing 0.200 mol of each gas in a 5.00 L container. What will be the equilibrium concentration of each gas? How will the concentrations then change if 0.050 mol of NO_2 is added to the equilibrium mixture?

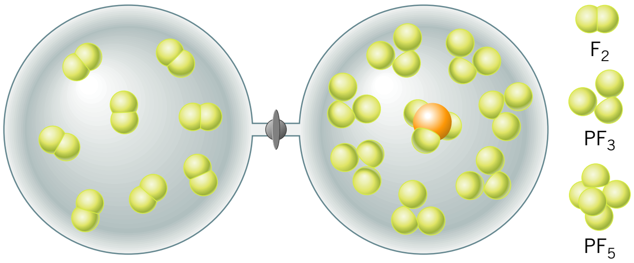
***15.82** At a certain temperature, $K_c = 0.914$ for the reaction

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

Equal amounts of NO and NO_2 are to be placed in a 5.00 L container until the N_2O concentration at equilibrium is 0.0500 *M*. How many moles of NO and NO_2 must be placed in the container?

15.83 Two 1.00 L bulbs are filled with 0.500 atm of $F_2(g)$ and $PF_3(g)$, respectively, as illustrated in the figure below. At a particular temperature, $K_P = 4.0$ for the reaction of these gases to form $PF_5(g)$:

$$F_2(g) + PF_3(g) \rightleftharpoons PF_5(g)$$



(a) The stopcock between the bulbs is opened and the pressure falls. Make a sketch of this apparatus showing the gas composition once the pressure is stable.

(b) List any chemical reactions that continue to occur once the pressure is stable.

(c) Suppose all the gas in the left bulb is forced into the bulb on the right and then the stopcock is closed. Make a second sketch to show the composition of the gas mixture after equilibrium is reached. Comment on how the composition of the one-bulb system differs from that for the two-bulb system.

OH **15.84** For the equilibrium

$$3NO_2(g) \rightleftharpoons N_2O_5(g) + NO(g)$$

$K_c = 1.0 \times 10^{-11}$. If a 4.00 L container initially holds 0.20 mol of NO_2, how many moles of N_2O_5 will be present when this system reaches equilibrium?

15.85 To study the following reaction at 20 °C,

$$NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_2(g)$$

a mixture of $NO(g)$, $NO_2(g)$, and $H_2O(g)$ was prepared in a 10.0 L glass bulb. For NO, NO_2, and HNO_2, the initial concentrations were as follows: $[NO] = [NO_2] = 2.59 \times 10^{-3}$ *M* and $[HNO_2] = 0.0$ *M*. The initial partial pressure of $H_2O(g)$ was 17.5 torr. When equilibrium was reached, the HNO_2 concentration was 4.0×10^{-4} *M*. Calculate the equilibrium constant, K_c, for this reaction.

15.86 At 100.0 °C, $K_c = 0.135$ for the reaction

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

In a reaction mixture at equilibrium at this temperature, $[NH_3] = 0.030$ *M* and $[N_2] = 0.50$ *M*. What are the partial pressures of all of the gases in the mixture? Use them to calculate K_P and compare the result with K_P calculated using Equation 15.9.

Multi-Concept Problems

***15.87** For the reaction below, $K_P = 1.6 \times 10^6$ at 400.0 °C.

$$HCHO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

A mixture of $CO(g)$ and $H_2O(l)$ was prepared in a 2.00 L reaction vessel at 25 °C in which the pressure of CO was 0.177 atm. The mixture also contained 0.391 g of H_2O. The vessel was sealed and heated to 400 °C. When equilibrium was reached, what was the partial pressure of the $HCHO_2$ at 400 °C?

***15.88** At 2000 °C, the decomposition of CO_2,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

has $K_c = 6.4 \times 10^{-7}$. If a 1.00 L container holding 1.00×10^{-2} mol of CO_2 is heated to 2000 °C, what will be the partial pressure of CO (in atmospheres) at equilibrium? How many molecules of O_2 are present at equilibrium? How, if at all, does the density of the mixture change as it goes from its initial condition to its equilibrium state? How much heat, in joules, is absorbed or evolved in the approach to equilibrium?

***15.89** At 460 °C, the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has $K_c = 85.0$. If 0.0255 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO, and 0.0446 mol of SO_3 are placed in a 10.0 L container at this temperature, how many grams of each gas will be present when the mixture reaches equilibrium? What will the total pressure of the system be at equilibrium?

***15.90** At 200.0 °C, $K_c = 1.4 \times 10^{-10}$ for the reaction

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$$

If 300 mL of NO measured at 800 torr and 25 °C is placed in a 4.00 L container, what will be the N_2O and NO molar concentrations at equilibrium? What will be the total pressure of the mixture (in torr) at equilibrium?

*__15.91__ At 400 °C, $K_c = 2.9 \times 10^4$ for the reaction

$$HCHO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

A mixture was prepared with the following initial concentrations: [CO] = 0.20 *M*, $[H_2O] = 0.30$ *M*. No formic acid, $HCHO_2$, was initially present. What was the equilibrium concentration of $HCHO_2$? What is the density of the equilibrium mixture?

*__15.92__ The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ has $K_P = 0.140$ at 25.0 °C. Into a 4.50 L reaction vessel at this temperature was placed 0.0245 mol N_2O_4 and 0.0116 mol N_2O. What will be the density of the gas mixture (in units of gram per liter) **(a)** before the reaction starts, and **(b)** at equilibrium?

Exercises in Critical Thinking

15.93 In an equilibrium law, coefficients in the balanced equation appear as exponents on concentrations. Why, in general, does this not also apply for rate laws?

15.94 Why are equilibrium concentrations useful to know?

15.95 Suppose we set up a system in which water is poured into a vessel having a hole in the bottom. If the rate of water inflow is adjusted so that it matches the rate at which water drains through the hole, the amount of water in the vessel remains constant over time. Is this an equilibrium system? Explain.

15.96 Do equilibrium laws apply to other systems outside of chemistry? Give examples.

15.97 What might prevent a system from reaching dynamic equilibrium? Illustrate your answer with examples.

15.98 After many centuries the earth's atmosphere still has not come to equilibrium with the oceans and land. What factors are responsible for this?

15.99 If a mixture consisting of many small crystals in contact with a saturated solution is studied for a period of time, the smallest of the crystals are observed to dissolve while the larger ones grow even larger. Explain this phenomenon in terms of a dynamic equilibrium.

16 Acids and Bases, A Molecular Look

Chapter Outline

16.1 | Brønsted–Lowry Definition of Acids and Bases

16.2 | Strengths of Brønsted–Lowry Acids and Bases

16.3 | Periodic Trends in the Strengths of Acids

16.4 | Lewis Definition of Acids and Bases

16.5 | Acid–Base Properties of Elements and Their Oxides

16.6 | Advanced Ceramics and Acid–Base Chemistry

The chief method for making steel is called the basic oxygen process, in which pure oxygen is blown through a molten mixture of scrap steel and iron formed from iron ore in a blast furnace. The oxygen burns off excess carbon and oxidizes impurities such as silicon to oxides, like SiO_2. Calcium and magnesium oxide is added to combine with the SiO_2 to form molten slag, a process that involves an acid–base reaction. However, to describe this reaction adequately requires that we redefine acids and bases in a broader way that does not involve water or hydrogen ions. Such a definition is one of the topics discussed in this chapter. © AP/Wide World Photos.

This Chapter in Context

In Chapter 5 we introduced you to compounds that we call acids and bases. Many common substances, from household products such as vinegar and ammonia, to biologically important compounds such as amino acids, are conveniently classified as either an acid or a base. The significant property that makes such classifications useful is that *acids react with bases*. In fact, this is such a useful relationship that the acid–base concept has been expanded far beyond the limited Arrhenius definition we discussed in Chapter 5. We now return to acid–base chemistry to learn about these broader and often more useful views.

At the same time, we will study how trends in the strengths of acids and bases correlate with the periodic table. We will use the principles developed in previous chapters to explain why one acid should be stronger than another. The ability to judge relative acid strengths is an important skill to bring to the study of organic chemistry. (In the next chapter we will assign a numerical value that helps us more precisely compare strengths of acids and bases.) And finally, we will examine a modern application of acid–base chemistry to the production of useful high-tech materials.

16.1 | Brønsted–Lowry Definition of Acids and Bases

In Chapter 5, an acid was described as a substance that produces H_3O^+ in water, whereas a base gives OH^-. An acid–base neutralization, according to Arrhenius, is a reaction in which an acid and a base combine to produce water and a salt. However, many reactions resemble neutralizations without involving H_3O^+, OH^-, or even H_2O. For example, when open bottles of concentrated hydrochloric acid and concentrated aqueous ammonia are placed side by side, a white cloud forms when the vapors from the two bottles mix (see Figure 16.1). The cloud consists of tiny crystals of ammonium chloride, which form when ammonia and hydrogen chloride gases, escaping from the open bottles, mix in air and react.

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

What's interesting is that this is the same net reaction that occurs when an aqueous solution of ammonia (a base) is neutralized by an aqueous solution of hydrogen chloride (an acid). Yet, the gaseous reaction doesn't fit the description of an acid–base neutralization according to the Arrhenius definition because there's no water involved.

If we look at both the aqueous and gaseous reactions, they do have something in common. Both involve the transfer of a *proton* (a hydrogen ion, H^+) from one particle to another.[1] In water, where HCl is completely ionized, the transfer is from H_3O^+ to NH_3, as we discussed on page 179. The ionic equation is shown below.

$$NH_3(aq) + H_3O^+(aq) + Cl^-(aq) \longrightarrow \underbrace{NH_4^+(aq) + Cl^-(aq)}_{\text{The ions of } NH_4Cl} + H_2O$$

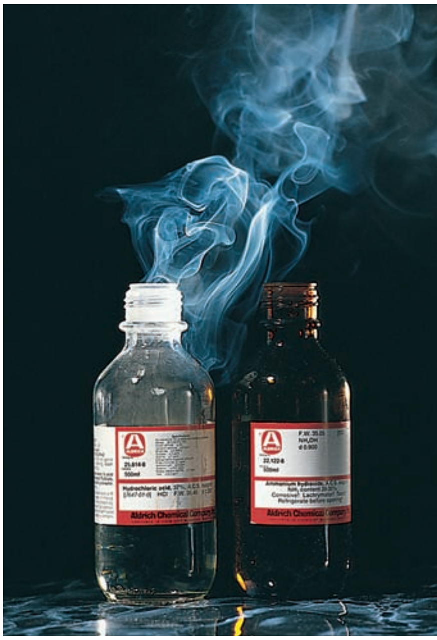


Figure 16.1 | **The reaction of gaseous HCl with gaseous NH_3.** As each gas escapes from its concentrated aqueous solution and mingles with the other, a cloud of microcrystals of NH_4Cl forms above the bottles. *(Andy Washnik)*

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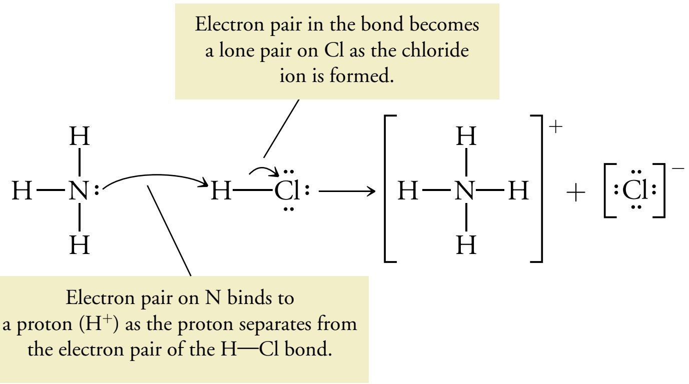
[1] When the single electron is removed from a hydrogen atom, what remains is just the nucleus of the atom, which is a proton. Therefore, a hydrogen ion, H^+, consists of a proton, and the terms *proton* and *hydrogen ion* are often used interchangeably.

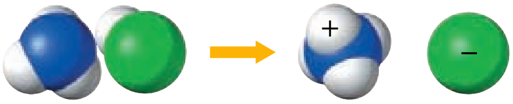
In the gas phase, the proton is transferred directly from the HCl molecule to the NH_3 molecule.

■ We are using "curved" arrows to show how electrons shift and rearrange during the formation of the ions. The electron pair on the nitrogen atom of the NH_3 molecule binds to H^+ as it is removed from the electron pair in the H—Cl bond. The electron pair in the H—Cl bond shifts entirely to the Cl as the Cl^- ion is formed.


Electron pair in the bond becomes a lone pair on Cl as the chloride ion is formed.

Electron pair on N binds to a proton (H^+) as the proton separates from the electron pair of the H—Cl bond.

■ Although the positive charge is shown on just one of the hydrogens in $NH_4{}^+$, it is actually spread equally over all four hydrogens.



As ammonium ions and chloride ions form, they attract each other, gather, and settle as crystals of ammonium chloride.

Proton Transfer Reactions

Johannes Brønsted (1879–1947), a Danish chemist, and Thomas Lowry (1874–1936), a British scientist, realized that the important event in most acid–base reactions is simply the transfer of a proton from one particle to another. Therefore, they redefined *acids* as substances that donate protons and *bases* as substances that accept protons. The heart of the *Brønsted–Lowry concept of acids and bases* is that *acid–base reactions are proton transfer reactions.* The definitions are therefore very simple.

TOOLS

Brønsted–Lowry definitions

Brønsted–Lowry Definitions of Acids and Bases[2]

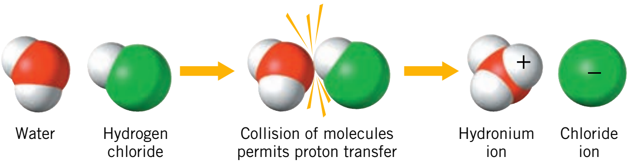
An **acid** is a proton donor.

A **base** is a proton acceptor.

Accordingly, hydrogen chloride is an acid because when it reacts with ammonia, HCl molecules donate protons to NH_3 molecules. Similarly, ammonia is a base because NH_3 molecules accept protons.

Even when water is the solvent, chemists use the Brønsted–Lowry definitions more often than those of Arrhenius. Thus, the reaction between hydrogen chloride and water to form hydronium ion (H_3O^+) and chloride ion (Cl^-), which is another proton transfer reaction, is clearly a Brønsted–Lowry acid–base reaction. Molecules of HCl are the acid in this reaction, and water molecules are the base. HCl molecules collide with water molecules and protons transfer during the collisions.

■ In H_3O^+, the positive charge is actually spread equally over all three hydrogens.



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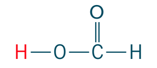
[2] Although Brønsted and Lowry are both credited with defining acids and bases in terms of proton transfer, Brønsted carried the concepts further. For the sake of brevity, we will often use the terms *Brønsted acid* and *Brønsted base* when referring to the substances involved in proton transfer reactions.

Conjugate Acids and Bases

Under the Brønsted–Lowry view, it is useful to consider any acid–base reaction as a chemical equilibrium, having both a forward and a reverse reaction. We first encountered a chemical equilibrium in a solution of a weak acid on page 170. Let's examine it again in the light of the Brønsted–Lowry definitions, using formic acid, $HCHO_2$, as an example. Because formic acid is a weak acid, we represent its ionization as a chemical equilibrium in which water is not just a solvent but also a chemical reactant, a proton acceptor.[3]

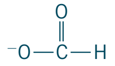
$$HCHO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$$



$$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}H$$

formic acid ($HCHO_2$)

Only the H in red is available in an acid–base reaction.



$$^{-}O{-}\overset{\overset{O}{\|}}{C}{-}H$$

formate ion (CHO_2^-)

In the forward reaction, a formic acid molecule donates a proton to the water molecule and changes to a formate ion, CHO_2^- (Figure 16.2*a*). Thus $HCHO_2$ behaves as a Brønsted acid, a proton donor. Because water accepts this proton from $HCHO_2$, water behaves as a Brønsted base, a proton acceptor.

Now let's look at the reverse reaction (Figure 16.2*b*). In it, H_3O^+ behaves as a Brønsted acid because it donates a proton to the CHO_2^- ion. The CHO_2^- ion behaves as a Brønsted base by accepting the proton.

The equilibrium involving $HCHO_2$, H_2O, H_3O^+, and CHO_2^- is typical of proton transfer equilibria in general, in that we can identify *two* acids (e.g., $HCHO_2$ and H_3O^+) and *two* bases (e.g., H_2O and CHO_2^-). Notice that in the aqueous formic acid equilibrium, the acid on the right of the arrows (H_3O^+) is formed from the base on the left (H_2O), and the base on the right (CHO_2^-) is formed from the acid on the left ($HCHO_2$).

Two substances that differ from each other only by one proton are referred to as a **conjugate acid–base pair**. Thus, H_3O^+ and H_2O are such a pair; they are alike except that H_3O^+ has one more proton than H_2O. One member of the pair is called the **conjugate acid** because it is the proton donor of the two. The other member is the **conjugate base** because it is the pair's proton acceptor. We say that *H_3O^+ is the conjugate acid of H_2O*, and *H_2O is the conjugate base of H_3O^+*. Notice that *the acid member of the pair has one more H^+ than the base member.*

TOOLS

Conjugate acid–base pairs

The pair $HCHO_2$ and CHO_2^- is the other conjugate acid–base pair in the aqueous formic acid equilibrium. $HCHO_2$ has one more H^+ than CHO_2^-, so the conjugate acid of CHO_2^- is $HCHO_2$; the conjugate base of $HCHO_2$ is CHO_2^-. One way to highlight

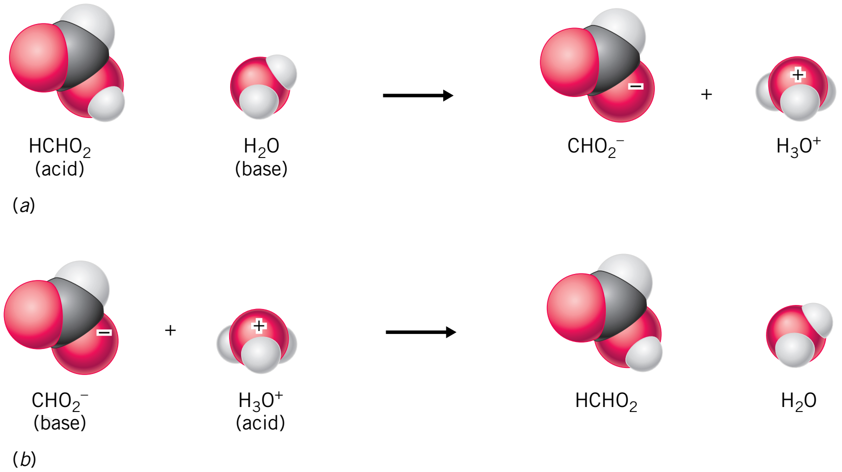


Figure 16.2 | **Brønsted–Lowry acids and bases in aqueous formic acid.** (*a*) Formic acid transfers a proton to a water molecule. $HCHO_2$ is the acid and H_2O is the base. (*b*) When hydronium ion transfers a proton to the CHO_2^- ion, H_3O^+ is the acid and CHO_2^- is the base.

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[3] Just as we have represented acetic acid as $HC_2H_3O_2$, placing the ionizable or acidic hydrogen first (as we do in HCl or HNO_3), so we give the formula of formic acid as $HCHO_2$ and the formula of the formate ion as CHO_2^-. As the chemical structure shows, however, the acidic hydrogen in formic acid is bonded to O, not C. Many chemists prefer to write formic acid as HCO_2H.

the two members of a conjugate acid–base pair in an equilibrium equation is to connect them by a line.

TOOLS

Conjugate acid–base equilibria

■ Notice how the conjugate acid always has one more H$^+$ than the conjugate base.

$$\overbrace{\underset{\text{acid}}{HCHO_2} + \underbrace{\underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+}}_{\text{conjugate pair}} + \underset{\text{base}}{CHO_2^-}}^{\text{conjugate pair}} \tag{16.1}$$

In any Brønsted–Lowry acid–base equilibrium, there are invariably *two* conjugate acid–base pairs. It is important that you learn how to pick them out of an equation by inspection and to write them from formulas.

Example 16.1
Determining the Formulas of Conjugate Acids and Bases

What is the conjugate base of nitric acid, HNO_3, and what is the conjugate acid of the hydrogen sulfate ion, HSO_4^-?

■ **Analysis:** Any reference to a conjugate acid or a conjugate base signals that the problem involves the Brønsted–Lowry acid–base concept. The key to answering the questions posed here is knowing the definitions, so be sure you've learned them.

■ **Assembling the Tools:** The tool required states that members of any conjugate acid–base pair differ by one (and *only* one) H$^+$, with the member having the greater number of hydrogens being the acid.

■ **Solution:** We are asked to find the conjugate base of HNO_3, which means HNO_3 must be the acid member of the pair. To find the formula of the base, we remove one H$^+$ from the acid. Removing one H$^+$ (both the atom and the charge) from HNO_3 leaves NO_3^-, so the nitrate ion is the conjugate base of HNO_3.

We are also asked to find the conjugate acid of HSO_4^-, so HSO_4^- must be the base member of an acid–base pair. To find the formula of the acid, we add one H$^+$ to the base, which is equivalent to adding one hydrogen to the formula of the base and increasing its positive charge (or decreasing its negative charge) by one unit. Adding an H$^+$ to HSO_4^- gives its conjugate acid, H_2SO_4.

■ **Are the Answers Reasonable?** As a check, we can quickly compare the two formulas in each pair.

$$\begin{array}{ll} HNO_3 & NO_3^- \\ H_2SO_4 & HSO_4^- \end{array}$$

In each case, the formula on the right has one less H$^+$ than the one on the left, so it is the conjugate base. We've answered the question correctly.

Practice Exercises

16.1 | Which of the following are conjugate acid–base pairs? Describe why the others are not true conjugate acid–base pairs. (a) H_3PO_4 and $H_2PO_4^-$, (b) HI and H$^+$, (c) NH_2^- and NH_3, (d) HNO_2 and NH_4^+, (e) CO_3^{2-} and CN^-, (f) HPO_4^{2-} and $H_2PO_4^-$. (*Hint:* Recall that conjugate acid–base pairs must differ by one H$^+$.)

16.2 | Write the formula of the conjugate base for each of the following Brønsted–Lowry acids: (a) H_2O, (b) HI, (c) HNO_2, (d) H_3PO_4, (e) $H_2PO_4^-$, (f) HPO_4^{2-}, (g) H_2S, (h) NH_4^+.

16.3 | Write the formula of the conjugate acid for each of the following Brønsted–Lowry bases: (a) HO_2^-, (b) SO_4^{2-}, (c) CO_3^{2-}, (d) CN^-, (e) NH_2^-, (f) NH_3, (g) $H_2PO_4^-$, (h) HPO_4^{2-}.

Example 16.2

Identifying Conjugate Acid–Base Pairs in a Brønsted–Lowry Acid–Base Reaction

The anion of sodium hydrogen sulfate, HSO_4^-, reacts as follows with the phosphate ion, PO_4^{3-}.

$$HSO_4^-(aq) + PO_4^{3-}(aq) \longrightarrow SO_4^{2-}(aq) + HPO_4^{2-}(aq)$$

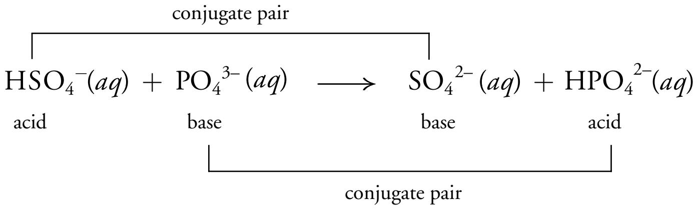
Identify the two conjugate acid–base pairs.

■ Sodium hydrogen sulfate (also called sodium bisulfate) is used to manufacture certain kinds of cement and to clean oxide coatings from metals.

■ **Analysis:** There are two things to look for in identifying the conjugate acid–base pairs in an equation. One is that the members of a conjugate pair are alike except for the number of hydrogens and the charge. The second is that the members of each pair must be on opposite sides of the arrow, as in Equation 16.1, and we cannot have both acids (or both bases) on the same side of the equation. In each pair, of course, the acid is the one with the greater number of hydrogens.

■ **Assembling the Tools:** We will use Equation 16.1 as a template to establish the relationships among the acid–base members of the two pairs.

■ **Solution:** Two of the formulas in the equation contain "PO_4," so they must belong to the same conjugate pair. The one with the greater number of hydrogens, HPO_4^{2-}, must be the Brønsted–Lowry acid, and the other, PO_4^{3-}, must be the Brønsted–Lowry base. Therefore, one conjugate acid–base pair is HPO_4^{2-} and PO_4^{3-}. The other two ions, HSO_4^- and SO_4^{2-}, belong to the second conjugate acid–base pair; HSO_4^- is the conjugate acid and SO_4^{2-} is the conjugate base.



■ **Is the Answer Reasonable?** A check assures us that we have fulfilled the requirements that each conjugate pair has one member on one side of the arrow and the other member on the opposite side of the arrow and that the members of each pair differ from each other by one (and *only* one) H^+.

Practice Exercises

16.4 | Sodium cyanide solution, when poured into excess hydrochloric acid, releases hydrogen cyanide as a gas. The reaction is

$$NaCN(aq) + HCl(aq) \longrightarrow HCN(g) + NaCl(aq)$$

Identify the conjugate acid–base pairs in this reaction. (*Hint:* It may be more obvious if the spectator ions are removed.)

16.5 | One kind of baking powder contains sodium bicarbonate and calcium dihydrogen phosphate. When water is added, a reaction occurs by the following net ionic equation.

$$HCO_3^-(aq) + H_2PO_4^-(aq) \longrightarrow H_2CO_3(aq) + HPO_4^{2-}(aq)$$

Identify the two Brønsted acids and the two Brønsted bases in this reaction. (The H_2CO_3 decomposes to release CO_2, which causes the cake batter to rise.)

16.6 | When some of the strong cleaning agent "trisodium phosphate" is mixed with household vinegar, which contains acetic acid, the following equilibrium is one of the many that are established. (The position of equilibrium lies to the right.) Identify the pairs of conjugate acids and bases.

$$PO_4^{3-}(aq) + HC_2H_3O_2(aq) \rightleftharpoons HPO_4^{2-}(aq) + C_2H_3O_2^-(aq)$$

Amphoteric Substances

Some molecules or ions are able to function either as an acid or as a base, depending on the kind of substance mixed with them. For example, in its reaction with hydrogen chloride, water behaves as a *base* because it *accepts* a proton from the HCl molecule.

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HCl(g)} \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

On the other hand, water behaves as an *acid* when it reacts with the weak base ammonia.

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Here, H_2O *donates* a proton to NH_3 in the forward reaction.

■ From the Greek *amphoteros,* "partly one and partly the other."

A substance that can be either an acid or a base depending on the other substance present is said to be **amphoteric.** Another term is **amphiprotic**, which stresses that the *proton* donating or accepting ability is of central concern.

Amphoteric or amphiprotic substances may be either molecules or ions. For example, anions of acid salts, such as the bicarbonate ion of baking soda, are amphoteric. The HCO_3^- ion can either donate a proton to a base or accept a proton from an acid. Thus, toward the hydroxide ion, the bicarbonate ion is an acid; it donates its proton to OH^-.

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{OH^-(aq)} \longrightarrow CO_3^{2-}(aq) + H_2O$$

Toward hydronium ion, however, HCO_3^- is a base; it accepts a proton from H_3O^+.

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)} \longrightarrow H_2CO_3(aq) + H_2O$$

[Recall that H_2CO_3 (carbonic acid) almost entirely decomposes to $CO_2(g)$ and water as it forms.]

Practice Exercises

16.7 | Which of the following are amphoteric and which are not? Provide reasons for your decisions. (a) $H_2PO_4^-$, (b) HPO_4^{2-}, (c) H_2S, (d) H_3PO_4, (e) NH_4^+, (f) H_2O, (g) HI, (h) HNO_2. (*Hint:* Amphoteric substances must be able to provide an H^+ and also react with an H^+.)

16.8 | The anion of sodium monohydrogen phosphate, Na_2HPO_4, is amphoteric. Using H_3O^+ and OH^-, write net ionic equations that illustrate this property.

16.2 | Strengths of Brønsted–Lowry Acids and Bases

Brønsted–Lowry acids and bases have differing abilities to lose or gain protons. In this section we examine how these abilities can be compared and how we can anticipate differences according to the locations of key elements in the periodic table.

Comparing Acids and Bases to a Relative Standard

When we speak of the strength of a Brønsted–Lowry acid, we are referring to its ability to donate a proton to a base. We measure this by determining the extent to which the reaction of the acid with the base proceeds toward completion—the more complete the reaction, the stronger the acid. To compare the strengths of a series of acids, we have to select some reference base, and because we are interested most in reactions in aqueous media, that base is usually water (although other reference bases could also be chosen).

In Chapter 5 we discussed strong and weak acids from the Arrhenius point of view, and much of what we said there applies when the same acids are studied using the Brønsted–Lowry concept. Thus, acids such as HCl and HNO_3 react completely with water to give H_3O^+ because they are strong proton donors. Hence, we classify them as *strong Brønsted–Lowry acids*. On the other hand, acids such as HNO_2 (nitrous acid) and $HC_2H_3O_2$ (acetic acid) are much weaker proton donors. Their reactions with water are far from complete, and we classify them as *weak acids*.

In a similar manner, the relative strengths of Brønsted *bases* are assigned according to their abilities to accept and bind protons. Once again, to compare strengths, we have to choose a standard acid. Because water is amphiprotic, it can serve as the standard acid as well. Substances that are powerful proton acceptors, such as the oxide ion, react completely and are considered to be *strong Brønsted–Lowry bases*.

$$O^{2-} + H_2O \xrightarrow{100\%} 2OH^-$$

Weaker proton acceptors, such as ammonia, undergo incomplete reactions with water; we classify them as *weak bases*.

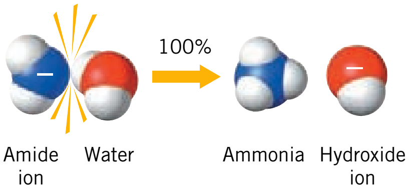
Hydronium Ion and Hydroxide Ion in Water

Both HCl and HNO_3 are very powerful proton donors. When placed in water they react completely, losing their protons to water molecules to yield H_3O^+ ions. Representing them by the general formula HA, we have

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \xrightarrow{100\%} \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{A^-}$$

Because both reactions go to completion, we really can't tell which of the two, HCl or HNO_3, is actually the better proton donor (stronger acid). This would require a reference base less willing than water to accept protons. In water, both HCl and HNO_3 converted quantitatively to another acid, H_3O^+. The conclusion, therefore, is that *H_3O^+ is the strongest acid we will ever find in an aqueous solution*, because stronger acids react completely with water to give H_3O^+.

A similar conclusion is reached regarding hydroxide ion. We noted that the strong Brønsted base O^{2-} reacts completely with water to give OH^-. Another very powerful proton acceptor is the amide ion, NH_2^-, which also reacts completely with water.



Of course, we can also express this reaction in the form of a regular chemical equation,

$$\underset{\text{base}}{NH_2^-} + \underset{\text{acid}}{H_2O} \xrightarrow{100\%} \underset{\text{acid}}{NH_3} + \underset{\text{base}}{OH^-}$$

Using water as the reference acid, we can't tell which is the better proton acceptor, O^{2-} or NH_2^-, because both react completely, being replaced by another base, OH^-. Therefore, we can say that *OH^- is the strongest base we will ever find in an aqueous solution*, because stronger bases react completely with water to give OH^-.

Comparing Acid–Base Strengths of Conjugate Pairs

The chemical equation for the ionization of an acid in water actually shows two Brønsted–Lowry acids. One is the acid itself and the other is hydronium ion. In almost every case, one of the acids is stronger than the other, and the position of equilibrium tells us which of the two acids is stronger. Let's see how this works using the acetic acid equilibrium, in which the position of equilibrium lies to the left.

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{C_2H_3O_2^-(aq)}$$

The two Brønsted–Lowry acids in this equilibrium are $HC_2H_3O_2$ and H_3O^+, and it's helpful to think of them as competing with each other in donating protons to acceptors. The fact that nearly all potential protons stay on the $HC_2H_3O_2$ molecules, and only a relative few spend their time on the H_3O^+ ions, means that the *hydronium ion is a better proton donor than the acetic acid molecule.* Thus, the hydronium ion is a stronger Brønsted–Lowry acid than acetic acid, and we inferred this relative acidity from the position of equilibrium.

The acetic acid equilibrium also has two bases, $C_2H_3O_2^-$ and H_2O. Both compete for any available protons. But at equilibrium, most of the protons originally carried by acetic acid are still found on $HC_2H_3O_2$ molecules; relatively few are joined to H_2O in the form of H_3O^+ ions. This means that *acetate ions must be more effective than water molecules at obtaining and holding protons from proton donors.* This is the same as saying that the acetate ion is a stronger base than the water molecule, a fact we are able to infer, once again, from the position of the acetic acid equilibrium.

The preceding analysis of the acetic acid equilibrium brings out an important point. Notice that both the weaker of the two acids and the weaker of the two bases are found on the same side of the equation, which is the side favored by the position of equilibrium.

TOOLS

Acid–base strength and the position of equilibrium

The position of an acid–base equilibrium favors the weaker acid and base.

$$\underset{\text{weaker acid}}{HC_2H_3O_2(aq)} + \underset{\text{weaker base}}{H_2O} \rightleftharpoons \underset{\text{stronger acid}}{H_3O^+(aq)} + \underset{\text{stronger base}}{C_2H_3O_2^-(aq)}$$

← *Position of equilibrium lies to the left, in favor of the weaker acid and base.*

Reciprocal Relationship in Acid–Base Strength

One aid in predicting the relative strengths of conjugate acids and bases is the existence of a reciprocal relationship.

TOOLS

Reciprocal relationship

The stronger a Brønsted acid is, the weaker is its conjugate base.

To illustrate, recall that HCl(g) is a very strong Brønsted acid; it's 100% ionized in a dilute aqueous solution.

$$HCl(g) + H_2O \xrightarrow{100\%} H_3O^+(aq) + Cl^-(aq)$$

As we explained in Chapter 5, we don't write double equilibrium arrows for the ionization of a strong acid. Not doing so with HCl is another way of saying that the chloride ion, the conjugate base of HCl, must be a very weak Brønsted–Lowry base. Even in the presence of H_3O^+, a very strong proton donor, chloride ions aren't able to win protons. So HCl, the strong acid, has a particularly weak conjugate base, Cl^-.

There's a matching reciprocal relationship.

The weaker a Brønsted acid is, the stronger is its conjugate base.

Consider, for example, the conjugate pair, OH^- and O^{2-}. The hydroxide ion is the conjugate acid and the oxide ion is the conjugate base. But the hydroxide ion must be an *extremely* weak Brønsted–Lowry acid; in fact, we've known it so far only as a base. Given the extraordinary weakness of OH^- as an acid, its conjugate base, the oxide ion, must be an exceptionally strong base. And as you've already learned, oxide ion is such a strong base that its reaction with water is 100% complete. That's why we don't write double equilibrium arrows in the equation for the reaction.

$$\underset{\text{base}}{O^{2-}} + \underset{\text{acid}}{H_2O} \xrightarrow{100\%} \underset{\text{acid}}{OH^-} + \underset{\text{base}}{OH^-}$$

The very strong base O^{2-} has
a very weak conjugate acid, OH^-.

An amphoteric substance will act as a base if mixed with an acid, but it will act as an acid if mixed with a base. You might ask: If two amphoteric substances are mixed together, which will act as the acid and which as the base? The obvious answer is that the stronger acid will act as the acid and the other will be the base. In the reaction below, we find that the position of equilibrium lies to the left (with the reactants).

$$\underset{\text{acid}}{H_2S(aq)} + \underset{\text{base}}{HCO_3^-(aq)} \rightleftharpoons \underset{\text{base}}{HS^-(aq)} + \underset{\text{acid}}{H_2CO_3(aq)}$$

$\longleftarrow$

Position of equilibrium lies to the left.
HCO_3^- must be a weaker base than HS^-.

This can be interpreted as meaning that $H_2CO_3(aq)$ is a stronger acid than $H_2S(aq)$, which in turn makes $HCO_3^-(aq)$ a weaker base than $HS^-(aq)$. Therefore, if we mix a solution containing $HS^-(aq)$ with a solution containing $HCO_3^-(aq)$, the reaction will be

$$\underset{\text{base}}{HS^-(aq)} + \underset{\text{acid}}{HCO_3^-\,(aq)} \rightleftharpoons \underset{\text{acid}}{H_2S\,(aq)} + \underset{\text{base}}{CO_3^{2-}(aq)}$$

because the stronger base, HS^-, will remove the H^+ from the weaker base, HCO_3^-, causing the latter to actually behave as an acid.

Example 16.3

Using Reciprocal Relationships to Predict Equilibrium Positions

In the reaction below, will the position of equilibrium lie to the left or to the right, given the fact that acetic acid is known to be a stronger acid than the hydrogen sulfite ion?

$$HSO_3^-(aq) + C_2H_3O_2^-(aq) \rightleftharpoons HC_2H_3O_2(aq) + SO_3^{2-}(aq)$$

■ **Analysis:** In the equation above, the two acids are $HC_2H_3O_2$ and HSO_3^-. To find the answer to the question posed in the problem, we have to ask: How are the relative strengths of the acids related to where the position of equilibrium will be? The tools we select must relate to this issue.

■ **Assembling the Tools:** The position of an acid–base equilibrium favors the weaker acid and base. That's one of the tools we need to solve this problem. The other is the reciprocal relationship between the strengths of the members of a conjugate acid–base pair.

■ **Solution:** We'll write the equilibrium equation, using the given fact about the relative strengths of acetic acid and the hydrogen sulfite ion to start writing labels.

$$\underset{\text{weaker acid}}{HSO_3^-(aq)} + C_2H_3O_2^-(aq) \rightleftharpoons \underset{\text{stronger acid}}{HC_2H_3O_2(aq)} + SO_3^{2-}(aq)$$

Now we'll use our tool about the reciprocal relationships to label the two bases. The stronger acid must have the weaker conjugate base; the weaker acid must have the stronger conjugate base.

$$\underset{\text{weaker acid}}{HSO_3^-(aq)} + \underset{\text{weaker base}}{C_2H_3O_2^-(aq)} \rightleftharpoons \underset{\text{stronger acid}}{HC_2H_3O_2(aq)} + \underset{\text{stronger base}}{SO_3^{2-}(aq)}$$

Finally, because the position of equilibrium favors the weaker acid and base, the position of equilibrium lies to the left.

■ **Is the Answer Reasonable?** There are two things we can check. First, both of the weaker conjugates should be on the same side of the equation. They are, so that suggests we've made the correct assignments. Second, the reaction will proceed farther in the direction of the weaker acid and base, so that places the position of equilibrium on the left, which agrees with our answer.

Practice Exercises

16.9 | Given that HSO_4^- is a stronger acid than HPO_4^{2-}, what is the chemical reaction if solutions containing these ions are mixed together? (*Hint:* One of these must act as an acid and the other as a base.)

16.10 | Given that HSO_4^- is a stronger acid than HPO_4^{2-}, determine whether the substances on the left of the arrows or those on the right are favored in the following equilibrium.

$$HSO_4^-(aq) + PO_4^{3-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HPO_4^{2-}(aq)$$

16.3 | Periodic Trends in the Strengths of Acids

Table 16.1 Acidic Binary Compounds of Hydrogen and Nonmetals[a]

Group 6A
(H_2O)
H_2S Hydrosulfuric acid
H_2Se Hydroselenic acid
H_2Te Hydrotelluric acid
Group 7A
HF Hydrofluoric acid
*HCl Hydrochloric acid
*HBr Hydrobromic acid
*HI Hydroiodic acid

[a] The *names* are for the aqueous solutions of these compounds. Strong acids are indicated with asterisks.

In most cases, acids are formed by nonmetals, either in the form of solutions of their compounds with hydrogen [such as HCl(*aq*)] or as solutions of their oxides, which react with water to form oxoacids (such as H_2SO_4). The strengths of these acids vary in a systematic way with the location of the nonmetal in the periodic table.

Trends in the Strengths of Binary Acids

Many (but not all) of the binary compounds between hydrogen and nonmetals, which we may represent by HX and H_2X, are acidic and are called **binary acids**. Table 16.1 lists those that are acids in water. The strong acids are marked by asterisks.

The relative strengths of binary acids correlate with the periodic table in two ways.

TOOLS

Periodic trends in strengths of binary acids

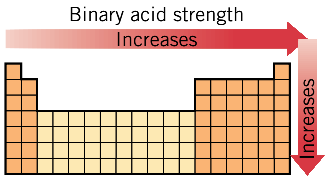
The strengths of the binary acids increase from left to right within the same period.
The strengths of binary acids increase from top to bottom within the same group.

Two factors can account for these variations. One is the electronegativity of the nonmetal X, and the other is the strength of the H—X bond.

Variations in electronegativity of the atom X alter the polarity of the H—X bond, so as X becomes more electronegative, the partial positive charge ($\delta+$) on H becomes greater. This makes it easier for the hydrogen to separate as H^+, so the molecule becomes a better proton donor.

A major influence on acidity is the strength of the H—X bond. Breaking this bond is essential for the hydrogen to separate as an H^+ ion, so anything that contributes to variations in bond strength will also affect variations in acid strength.

Going from left to right across a period, atomic size varies little, so the strengths of the H—X bonds are nearly the same. The major influence is the variation in the electronegativity of X, which increases from left to right. For example, as we go from left to right within Period 3, from S to Cl, the electronegativity increases and we find that HCl is a stronger acid than H_2S. A similar increase in electronegativity occurs going left to right in Period 2, from O to F, so HF is a stronger acid than H_2O.



In going down a group, there are two opposing factors. The electronegativity decreases, so the H—X bonds become less polar. At the same time, the atoms X become much larger, and this leads to a large drop in the H—X bond strength.[4] The variation in polarity tends to make the acids weaker, but the variation in bond strength tends to make them stronger. Changes in bond strength seem to win out, because the acids H_nX become stronger as we go down a group. For example, among the binary acids of the halogens the following order of relative acidity is observed.[5]

$$HF < HCl < HBr < HI$$

Thus, HF is the weakest acid in the series, and HI is the strongest. The identical trend occurs in the series of the binary acids of Group 6A elements, having formulas of the general type H_2X. Notice that these trends in acidity are the opposite of what we would expect on the basis of trends in electronegativities, which tell us that the H—F bond is more polar than the H—I bond and that the O—H bond is more polar than the H—S bond.

Practice Exercises

16.11 | Order the following groups of acids from the weakest to the strongest: (a) HI, HF, HBr; (b) HCl, PH_3, H_2S; (c) H_2Te, H_2O, H_2Se; (d) AsH_3, HBr, H_2Se; (e) HI, PH_3, H_2Se. (*Hint:* These are all binary acids.)

16.12 | Using *only* the periodic table, choose the stronger acid of each pair: (a) H_2Se or HBr, (b) H_2Se or H_2Te, (c) H_2O or H_2S.

Trends in the Strengths of Oxoacids

In Chapter 5 you learned that acids composed of hydrogen, oxygen, and some other element are called **oxoacids** (see Table 16.2). Those that are strong acids in water are identified in the table by asterisks.

Table 16.2 **Some Oxoacids of Nonmetals and Metalloids**[a]

Group 4A	Group 5A	Group 6A	Group 7A
H_2CO_3 Carbonic acid	*HNO_3 Nitric acid HNO_2 Nitrous acid		HFO Hypofluorous acid
	H_3PO_4 Phosphoric acid H_3PO_3 Phosphorous acid[b]	*H_2SO_4 Sulfuric acid H_2SO_3 Sulfurous acid[c]	*$HClO_4$ Perchloric acid *$HClO_3$ Chloric acid $HClO_2$ Chlorous acid HClO Hypochlorous acid
	H_3AsO_4 Arsenic acid H_3AsO_3 Arsenous acid	*H_2SeO_4 Selenic acid H_2SeO_3 Selenous acid	*$HBrO_4$ Perbromic acid[d] *$HBrO_3$ Bromic acid
		$Te(OH)_6$ Telluric acid[e] H_2TeO_3 Tellurous acid	HIO_4 Periodic acid (H_5IO_6)[f] HIO_3 Iodic acid

[a] Strong acids are indicated with asterisks.

[b] Phosphorous acid, despite its formula, is only a diprotic acid.

[c] Hypothetical. An aqueous solution actually contains just dissolved sulfur dioxide, $SO_2(aq)$.

[d] Pure perbromic acid is unstable; a dihydrate is known.

[e] $Te(OH)_6$ is a diprotic acid.

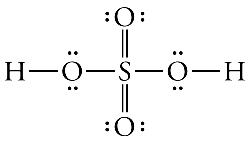
[f] H_5IO_6 is formed from $HIO_4 + 2H_2O$.

---

[4] Small atoms tend to form stronger bonds than large atoms, so as we go down a group there is a rapid decrease in the H—X bond strength as the atoms X become larger.

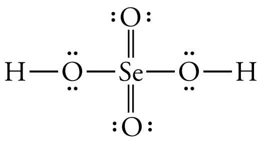
[5] We compare acid strengths by the acid's ability to donate a proton to a particular base. As we noted earlier, for strong acids such as HCl, HBr, and HI, water is too strong a proton acceptor to permit us to see differences among their proton-donating abilities. All three of these acids are completely ionized in water and so appear to be of equal strength, a phenomenon called the *leveling effect* (the differences are obscured or *leveled* out). To compare the acidities of these acids, a solvent that is a weaker proton acceptor than water (liquid HF or $HC_2H_3O_2$, for example) has to be used.

A feature common to the structures of all oxoacids is the presence of O—H groups bonded to some central atom. For example, the structures of two oxoacids of the Group 6A elements are



H_2SO_4

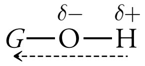
sulfuric acid



H_2SeO_4

selenic acid

When an oxoacid ionizes, the hydrogen that's lost as an H^+ comes from the same kind of bond in every instance—specifically, an O—H bond. The "acidity" of such a hydrogen, meaning the ease with which it's released as H^+, is determined by how the group of atoms attached to the oxygen affects the polarity of the O—H bond. If this group of atoms makes the O—H bond more polar, it will cause the H to come off more easily as H^+ and thereby increase the acidity of the molecule.



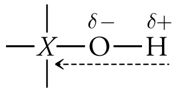
$G-\overset{\delta-}{O}-\overset{\delta+}{H}$

If the group of atoms, *G*, attached to the O—H group is able to draw electron density from the O atom, the O will pull electron density from the O—H bond, thereby making the bond more polar.

It turns out that there are two principal factors that determine how the polarity of the O—H bond is affected. One is the electronegativity of the central atom in the oxoacid and the other is the number of oxygens attached to the central atom.

Effect of the Electronegativity of the Central Atom

To study the effects of the electronegativity of the central atom, we must compare oxoacids having the same number of oxygens. When we do this, we find that as the electronegativity of the central atom increases, the oxoacid becomes a better proton donor (i.e., a stronger acid). The following diagram illustrates the effect.



$-\underset{|}{\overset{|}{X}}-\overset{\delta-}{O}-\overset{\delta+}{H}$

As the electronegativity of *X* increases, electron density is drawn away from O, which draws electron density away from the O—H bond. This makes the bond more polar and makes the molecule a better proton donor.

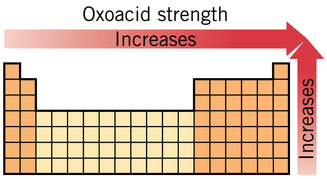
TOOLS

Trends in the strengths of oxoacids

Because electronegativity increases from bottom to top within a group and from left to right within a period, we can make the following generalization.

> When the central atoms of oxoacids hold the same number of oxygen atoms, the acid strength increases from bottom to top within a group and from left to right within a period.

In Group 6A, for example, H_2SO_4 is a stronger acid than H_2SeO_4 because sulfur is more electronegative than selenium. Similarly, among the halogens, acid strength increases for acids with the formula HXO_4 as follows:



$$HIO_4 < HBrO_4 < HClO_4$$

Going from left to right within Period 3, we can compare the acids H_3PO_4, H_2SO_4, and $HClO_4$, where we find the following order of acidities.

$$H_3PO_4 < H_2SO_4 < HClO_4$$

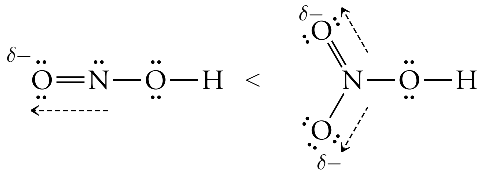
Practice Exercises

16.13 | Which is the stronger acid: (a) $HClO_3$ or $HBrO_3$, (b) H_3PO_4 or H_2SO_4? (*Hint:* Note that each pair has the same number of oxygen atoms.)

16.14 | In each pair indicate the weaker acid: (a) H_3PO_4 or H_3AsO_4, (b) HIO_4 or H_2TeO_4.

Effect of the Number of Oxygens Bound to the Central Atom

Comparing oxoacids with the same central atom, we find that as the number of *lone oxygens* increases, the oxoacid becomes a better proton donor. (A *lone oxygen* is one that is bonded only to the central atom and not to a hydrogen.) Thus, comparing HNO_3 with HNO_2, we find that HNO_3 is the stronger acid. To understand why, let's look at their molecular structures.



nitrous acid nitric acid

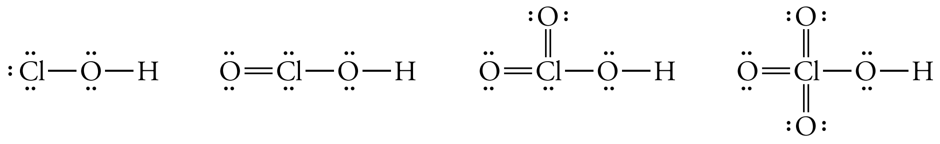
In an oxoacid, lone oxygens pull electron density away from the central atom, which increases the central atom's ability to draw electron density away from the O—H bond. It's as though the lone oxygens make the central atom more electronegative. Therefore, the more lone oxygens that are attached to a central atom, the more polar will be the O—H bonds of the acid and the stronger will be the acid. Thus, the two lone oxygens in HNO_3 produce a greater effect than the one lone oxygen in HNO_2, so HNO_3 is the stronger acid.

■ Oxygen is the second most electronegative element and has a strong tendency to pull electron density away from any atom to which it is attached.

Similar effects are seen among other oxoacids, as well. For the oxoacids of chlorine, for instance, we find the following trend:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Comparing their structures, we have



HClO HClO$_2$ HClO$_3$ HClO$_4$

■ Usually, the formula for hypochlorous acid is written HOCl to reflect its molecular structure. We've written it HClO here to make it easier to follow the trend in acid strengths among the oxoacids of chlorine.

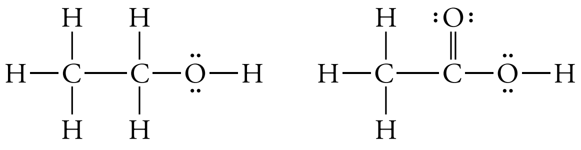
This leads to another generalization.

> For a given central atom, the acid strength of an oxoacid increases with the number of oxygens held by the central atom.

TOOLS

Trends in the strengths of oxoacids

The ability of lone oxygens to affect acid strength extends to organic compounds as well. For example, compare the molecules below.

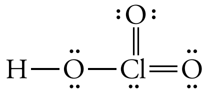


ethanol acetic acid

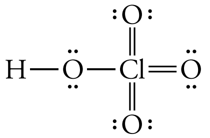
In water, ethanol (ethyl alcohol) is not acidic at all. Replacing the two hydrogens on the carbon adjacent to the OH group with an oxygen, however, yields acetic acid. The greater ability of oxygen to pull electron density from the carbon produces a greater polarity of the O—H bond, which is one factor that causes acetic acid to be a better proton donor than ethanol.

The Reciprocal Relationship—A Molecular Interpretation

On page 748 we noted the reciprocal relationship between the strength of an acid and that of its conjugate base. For oxoacids, the lone oxygens play a part in determining the basicity of the anion formed in the ionization reaction. Consider the acids $HClO_3$ and $HClO_4$.

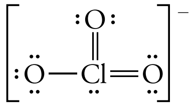


$HClO_3$

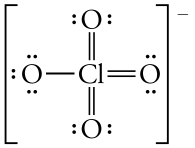


$HClO_4$

From our earlier discussion, we expect $HClO_4$ to be a stronger acid than $HClO_3$, which it is. Ionizations of their protons yield the anions ClO_3^- and ClO_4^-.



ClO_3^-



ClO_4^-

In an **oxoanion** (an anion formed from an oxoacid) the *lone* oxygens carry most of the negative charge, which is delocalized over the lone oxygens. In the ClO_3^- ion, the single negative charge is spread over three oxygens, so each carries a charge of about $\frac{1}{3}-$. This is not a *formal* charge obtained by the rules on page 389. We're saying that the 1− charge on the ion is delocalized over three oxygens to give each an actual charge of $\frac{1}{3}-$. By the same reasoning, in the ClO_4^- ion each oxygen carries a charge of about $\frac{1}{4}-$. The smaller negative charge on the oxygens in ClO_4^- makes this ion less able than ClO_3^- to attract H^+ ions from H_3O^+, so ClO_4^- is a weaker base than ClO_3^-. Thus, the anion of the stronger acid is the weaker base.

■ The concept of delocalization of electrons to provide stability was presented in Section 10.8.

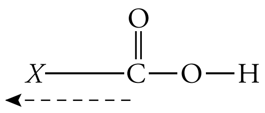
Practice Exercises

16.15 | In each pair, select the stronger acid: (a) HIO_3 or HIO_4, (b) H_2TeO_3 or H_2TeO_4, (c) H_3AsO_3 or H_3AsO_4. (*Hint:* This problem focuses on the effect of oxygen atoms in acids.)

16.16 | In each pair, select the weaker acid: (a) H_2SO_4 or $HClO_4$, (b) H_3AsO_4 or H_2SO_4.

Strengths of Organic Acids

On page 753 we noted that replacing two H atoms in an alcohol by a lone oxygen causes the resulting molecule to be acidic. The acidity of the molecule can be increased further if other electronegative groups such as halogens are bonded to carbon atoms near the —CO_2H group of the acid. Such a group, labeled *X* below, pulls electron density from the carbon atom of the carboxyl group, further increasing the polarity of the O—H bond. This causes an increase in the acidity of the molecule.



$X\text{——}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}H$

As the ability of *X* to draw electrons away from C increases, the polarity of the O—H bond increases and the molecule becomes more acidic.

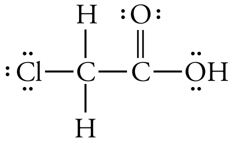
Thus, chloroacetic acid is a stronger acid than acetic acid, and dichloroacetic acid and trichloroacetic acids are increasingly stronger acids.

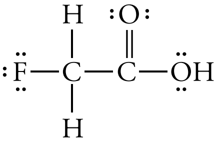
$$CH_3CO_2H < CH_2ClCO_2H < CHCl_2CO_2H < CCl_3CO_2H$$

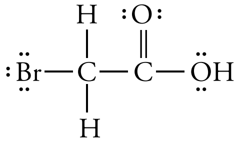
Addition of each chlorine effectively withdraws more electron density from the O—H bond, resulting in a weaker bond and a stronger acid.

Practice Exercises

16.17 | How would you expect the acidities of the following molecules to compare?

(a) 

(b) 

(c) 

16.4 | Lewis Definition of Acids and Bases

In our preceding discussions, acids and bases have been characterized by their tendency to lose or gain protons. However, there are many reactions not involving proton transfer that have properties we associate with acid–base reactions. For example, if gaseous SO_3 is passed over solid CaO, a reaction occurs in which $CaSO_4$ forms.

$$CaO(s) + SO_3(g) \longrightarrow CaSO_4(s) \qquad \textbf{(16.2)}$$

If these reactants are dissolved in water first, they react to form $Ca(OH)_2$ and H_2SO_4, and when their solutions are mixed the following reaction takes place.

$$Ca(OH)_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2H_2O \qquad \textbf{(16.3)}$$

The same two initial reactants, CaO and SO_3, form the same ultimate product, $CaSO_4$. It certainly seems that if Reaction 16.3 is an acid–base reaction, we should be able to consider Reaction 16.2 to be an acid–base reaction, too. But there are no protons being transferred, so our definitions require further generalizations. These were provided by G. N. Lewis, after whom Lewis symbols are named.

Lewis Definitions of Acids and Bases

1. A **Lewis acid** is any ionic or molecular species that can accept a pair of electrons in the formation of a coordinate covalent bond.
2. A **Lewis base** is any ionic or molecular species that can donate a pair of electrons in the formation of a coordinate covalent bond.
3. **Neutralization** is the formation of a coordinate covalent bond between the donor (base) and the acceptor (acid).

TOOLS

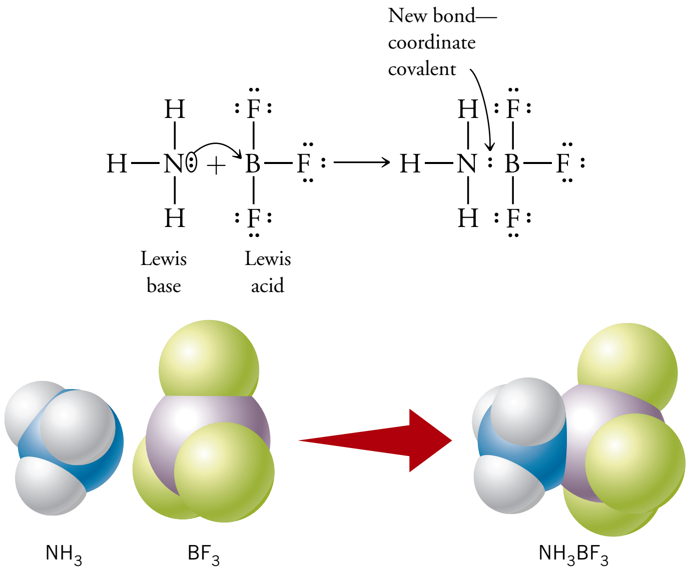
Lewis acid–base definitions

■ Remember, a coordinate covalent bond is just like any other covalent bond once it has formed. By using this term, we are following the origin of the electron pair that forms the bond.

Examples of Lewis Acid–Base Reactions

The reaction between BF_3 and NH_3 illustrates a Lewis acid–base neutralization. The reaction is exothermic because a bond is formed between N and B, with the nitrogen donating an electron pair and the boron accepting it.

■ A similar reaction was described in Chapter 9 between BCl_3 and ammonia. Compounds like BF_3NH_3, which are formed by simply joining two smaller molecules, are called **addition compounds.**



Note that as the bond forms from ammonia to boron trifluoride, the geometry around the boron changes from planar triangular to tetrahedral, which is what is expected with four bonds to the boron.

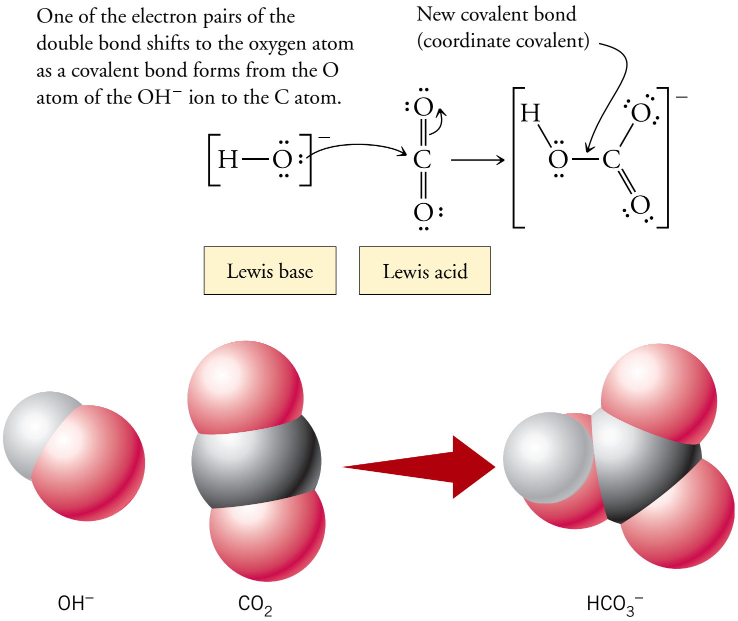
The ammonia molecule thus acts as a *Lewis base*. The boron atom in BF_3, having only six electrons in its valence shell and needing two more to achieve an octet, accepts the pair of electrons from the ammonia molecule. Hence, BF_3 is functioning as a *Lewis acid*.

As this example illustrates, Lewis bases are substances that have completed valence shells *and unshared pairs of electrons* (e.g., NH_3, H_2O, and O^{2-}). A Lewis acid, on the other hand, can be a substance with an incomplete valence shell, such as BF_3 or H^+.

A substance can also be a Lewis acid even when it has a central atom with a complete valence shell. This works when the central atom has a double bond that, by the shifting of an electron pair to an adjacent atom, can make room for an incoming pair of electrons from a Lewis base. Carbon dioxide is an example. When carbon dioxide is bubbled into aqueous sodium hydroxide, the gas is instantly trapped as the bicarbonate ion.

$$CO_2(g) + OH^-(aq) \longrightarrow HCO_3^-(aq)$$

Lewis acid–base theory represents the movement of electrons in this reaction as follows.



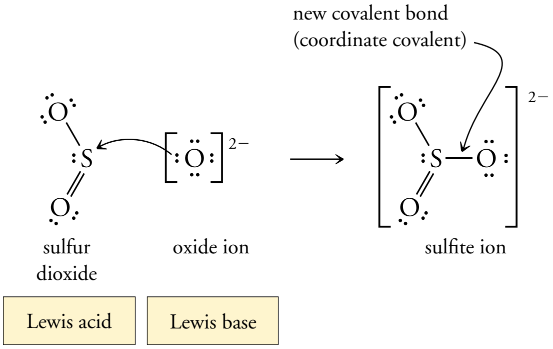
One of the electron pairs of the double bond shifts to the oxygen atom as a covalent bond forms from the O atom of the OH^- ion to the C atom.

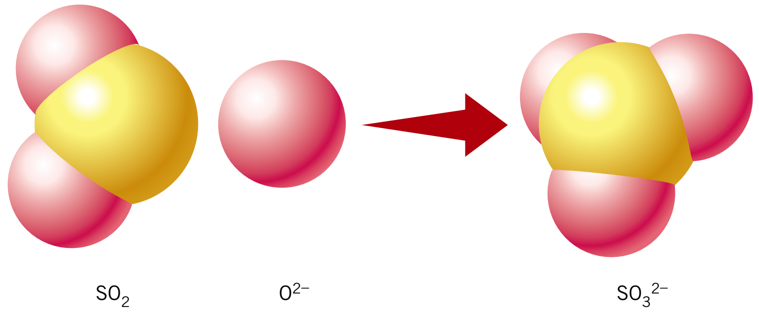
The donation of an electron pair *from* the oxygen of the OH^- ion produces a bond, so the OH^- ion is the Lewis base. The carbon atom of the CO_2 accepts the electron pair, so CO_2 is the Lewis acid.

Lewis acids can also be substances that have valence shells capable of holding more electrons. For example, consider the reaction of sulfur dioxide as a Lewis acid with oxide ion as a Lewis base to make the sulfite ion. This reaction occurs when gaseous sulfur dioxide, an acidic anhydride, mingles with solid calcium oxide, a basic anhydride, to give calcium sulfite, $CaSO_3$.

$$SO_2(g) + CaO(s) \longrightarrow CaSO_3(s)$$

Let's see how electrons relocate as the sulfite ion forms. We use one of the two resonance structures of SO_2 and one of the three such structures for the sulfite ion.





The two very electronegative oxygens attached to the sulfur in SO_2 give the sulfur a substantial positive partial charge, which induces the formation of the coordinate covalent bond from the oxide ion to the sulfur. In this case, sulfur can accommodate more than an octet in its valence shell, so relocation of electron pairs is not necessary.

In the chapter opening photograph we described some of the chemistry involved in steelmaking by the *basic oxygen process*. In this process, O_2 is blown through the molten steel mixture, causing carbon and other nonmetals to be oxidized. Silicon, for example, is oxidized to SiO_2 and must be removed from the steel. To accomplish this, calcium oxide is added that reacts with the silicon dioxide to form calcium silicate.

$$\underset{\text{calcium oxide}}{CaO(s)} + \underset{\text{silicon dioxide}}{SiO_2(l)} \longrightarrow \underset{\text{calcium silicate}}{CaSiO_3(l)}$$

This is a reaction between the Lewis base O^{2-} and the Lewis acid SiO_2. At the molecular level the reaction is complex because SiO_2 is the empirical formula for a polymeric oxide containing oxygen bridges between silicon atoms; the structure of the product is similarly complicated. At the high temperature of the furnace, the product is a liquid called *slag*, which is easily separated from the steel.

Table 16.3 summarizes the kinds of substances that behave as Lewis acids and bases. Study the table and then work on the Practice Exercises below.

Table 16.3 **Types of Substances that Are Lewis Bases**

Lewis Acids
Molecules or ions with incomplete valence shells (e.g., BF_3, H^+)
Molecules or ions with complete valence shells, but with multiple bonds that can be shifted to make room for more electrons (e.g., CO_2)
Molecules or ions that have central atoms capable of holding additional electrons (usually, atoms of elements in Periods 3 through 7) (e.g., SO_2)
Lewis Bases
Molecules or ions that have unshared pairs of electrons and that have complete valence shells (e.g., O^{2-}, NH_3)

Practice Exercises

16.18 | Identify the Lewis acid and base in each reaction.

(a) $NH_3 + H^+ \rightleftharpoons NH_4^+$

(b) $SeO_3 + Na_2O \rightleftharpoons Na_2SeO_4$

(c) $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

(*Hint:* Draw Lewis structures of the reactants.)

16.19 | (a) Is the fluoride ion more likely to behave as a Lewis acid or a Lewis base? Explain. (b) Is the $BeCl_2$ molecule more likely to behave as a Lewis acid or a Lewis base? Explain. (c) Is the SO_3 molecule more likely to behave as a Lewis acid or a Lewis base? Explain.

Interpreting Brønsted–Lowry Acid–Base Reactions Using the Lewis Acid–Base Concept

Reactions involving the transfer of a proton can be analyzed by either the Brønsted–Lowry or Lewis definitions of acids and bases. Consider, for example, the reaction between hydronium ion and ammonia in aqueous solution.

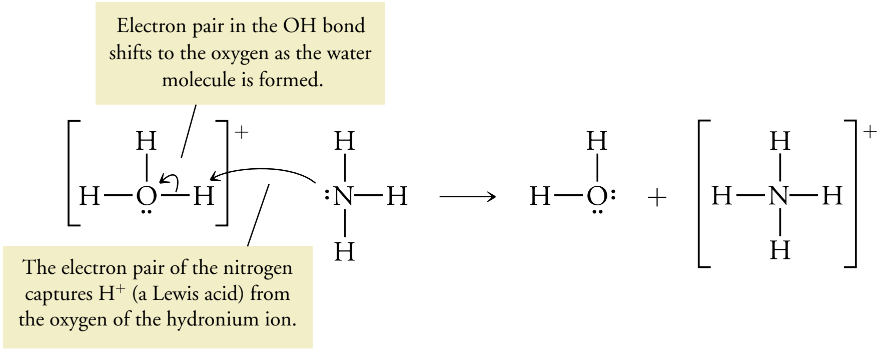
$$H_3O^+ + NH_3 \longrightarrow H_2O + NH_4^+$$

Applying the Brønsted–Lowry definitions, we have an acid, H_3O^+, reacting with a base, NH_3, to give the corresponding conjugates: H_2O being the conjugate base of H_3O^+ and NH_4^+ being the conjugate acid of NH_3.

To interpret this reaction using the Lewis definitions, we view it as the movement of a Lewis acid (the proton, H^+) from a weaker Lewis base (H_2O) to a stronger Lewis base (NH_3). In other words, we view the hydronium ion as the "neutralization" product of the Lewis base H_2O with the Lewis acid H^+. To emphasize that it is the proton that is transferring, we might write the equation as

$$H_2O{-}H^+ + NH_3 \longrightarrow H_2O + H^+{-}NH_3$$

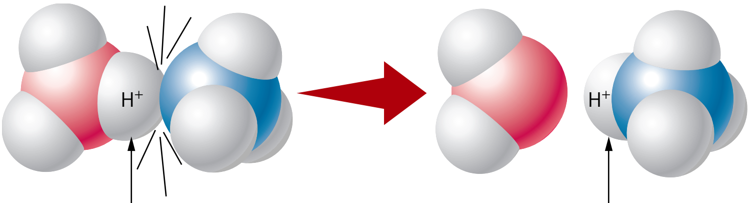
We can diagram this as follows using Lewis structures:



Electron pair in the OH bond shifts to the oxygen as the water molecule is formed.

The electron pair of the nitrogen captures H^+ (a Lewis acid) from the oxygen of the hydronium ion.

The molecular view of the reaction is



During a collision, a proton (Lewis acid) transfers from one Lewis base (water) to another Lewis base (ammonia).

In general, all Brønsted–Lowry acid–base reactions can be analyzed from the Lewis point of view following this same pattern, with the position of equilibrium favoring the proton being attached to the stronger Lewis base.

A word of caution is in order here. In analyzing proton transfer reactions, it is wise to stick to one interpretation or the other (Brønsted–Lowry or Lewis). Usually we will use the Brønsted–Lowry approach because it is useful to think in terms of conjugate acid–base pairs. However, if you switch to the Lewis interpretation, don't try to apply Brønsted–Lowry terminology at the same time; it won't work and you'll only get confused.

16.5 | Acid–Base Properties of Elements and Their Oxides

The elements most likely to form acids are the nonmetals in the upper right-hand corner of the periodic table. Those most likely to form basic hydroxides are similarly grouped in one general location in the table, among the metals, particularly those in Groups 1A (alkali metals) and 2A (alkaline earth metals). Thus, elements can themselves be classified according to their abilities to be involved in acids or bases.

In general, the experimental basis for classifying an element according to its abilities to form an acid or base depends on how its *oxide* behaves toward water. Earlier you learned that metal oxides like Na_2O and CaO are called *basic anhydrides* ("anhydride" means "without water") because they react with water to form hydroxides.

$$Na_2O + H_2O \longrightarrow 2NaOH \qquad \text{sodium hydroxide}$$
$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad \text{calcium hydroxide}$$

The reactions of metal oxides with water are really reactions of their oxide ions, which take H^+ from molecules of H_2O, leaving ions of OH^-.

Many metal oxides are insoluble in water, so their oxide ions are unable to take H^+ ions from H_2O molecules. Many are able to react with acids, which attack the oxide ions in the solid. Iron(III) oxide, for example, reacts with acid as follows.

$$Fe_2O_3(s) + 6H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 3H_2O$$

This is a common method for removing rust from iron in industrial processes.

Nonmetal oxides are usually *acidic anhydrides;* those that react with water give acidic solutions. Typical examples of the formation of acids from nonmetal oxides are the following reactions.

$$SO_3(g) + H_2O \longrightarrow H_2SO_4(aq) \qquad \text{sulfuric acid}$$
$$N_2O_5(g) + H_2O \longrightarrow 2HNO_3(aq) \qquad \text{nitric acid}$$
$$CO_2(g) + H_2O \longrightarrow H_2CO_3(aq) \qquad \text{carbonic acid}$$

Acidity of Hydrated Metal Ions

■ The force of attraction between an ion and water molecules is often strong enough to persist when the solvent water evaporates. Solid *hydrates* crystallize from solution, for example, $CuSO_4 \cdot 5H_2O$ (page 14).

When an ionic compound dissolves in water, molecules of the solute gather around the ions and we say the ions are *hydrated*. Within a hydrated cation, the metal ion behaves as a Lewis acid, binding to the partial negative charges on the oxygens of the surrounding water molecules, which serve as Lewis bases. Hydrated metal ions themselves tend to be Brønsted acids because of the equilibrium shown below. For simplicity, the equation represents a metal ion as a *mono*hydrate—namely, $M(H_2O)^{n+}$ with a net positive charge of $n+$ (n being 1, 2, or 3, depending on M).

$$M(H_2O)^{n+} + H_2O \rightleftharpoons MOH^{(n-1)+} + H_3O^+$$

In other words, hydrated metal ions tend to be proton donors in water. Let's see why.

The positive charge on the metal ion attracts the water molecule and draws electron density from the O—H bonds, causing them to become more polar (Figure 16.3). This increases the partial positive charge on H and weakens the O—H bond with respect to the transfer of H^+ to another nearby water molecule in the formation of a hydronium ion. The entire process can be illustrated as follows.

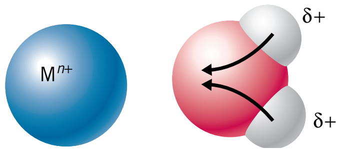
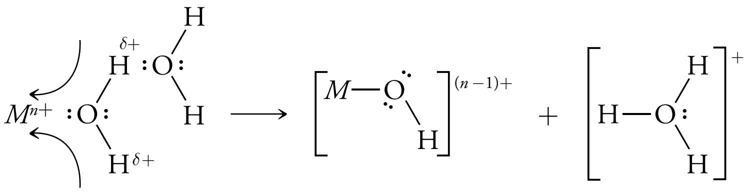
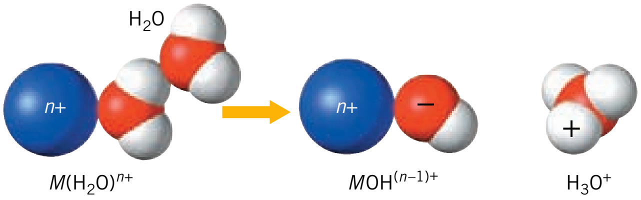


Figure 16.3 | **Polarization of a water molecule by a metal cation.** The positive charge on the metal ion pulls electron density away from the H atoms of the water molecule. This increases the partial positive charge on the H atoms and makes them easier to transfer to another H_2O molecule nearby.



Electron density is reduced in the O—H bonds of water (indicated by the curved arrows) by the positive charge of the metal ion, thereby increasing the partial positive charge on the hydrogens. This promotes the transfer of H^+ to a water molecule.



The degree to which metal ions produce acidic solutions depends primarily on two things: the amount of charge on the metal ion and the metal ion's size. As the metal ion's charge increases, the polarizing effect is increased, which thereby favors the release of H^+. This means that highly charged metal ions ought to produce solutions that are more acidic than ions of lower charge, and that is generally the case.

The size of the cation also affects its acidity because when the cation is small, the positive charge is highly concentrated. A highly concentrated positive charge is better able to pull electrons from an O—H bond than a positive charge that is more spread out. Therefore, for a given positive charge, the smaller the cation, the more acidic are its solutions.

Both size and amount of charge can be considered simultaneously by referring to a metal ion's *positive charge density*, the ratio of the positive charge to the volume of the cation (its ionic volume).

$$\text{Charge density} = \frac{\text{ionic charge}}{\text{ionic volume}}$$

Acidity of metal cations

The higher the positive charge density, the more effective the metal ion is at drawing electron density from the O—H bond and the more acidic is the hydrated cation.

Very small cations with large positive charges have large positive charge densities and tend to be quite acidic. An example is the hydrated aluminum ion, Al^{3+}. The hexahydrate, $Al(H_2O)_6^{3+}$, is one of several of this cation's hydrated forms that are present in an aqueous

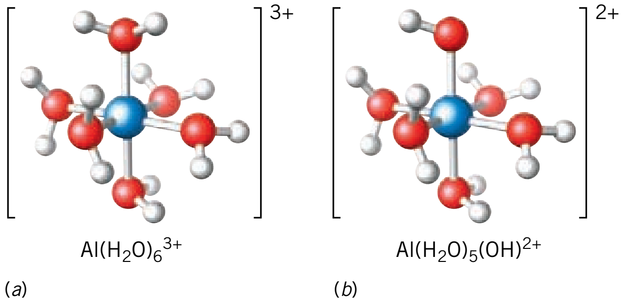


Figure 16.4 | **Hydrated aluminum ion is a weak proton donor in water.** (*a*) The highly charged Al^{3+} ion (blue) binds six water molecules in an aqueous solution to give an octahedral structure with the formula $Al(H_2O)_6{}^{3+}$. (*b*) When it donates a proton, the ion loses one unit of positive charge as a water molecule is transformed into a hydroxide ion, shown at the top of the structure. The resulting ion now has the formula $Al(H_2O)_5(OH)^{2+}$.

solution of an aluminum salt (see Figure 16.4). The ion is acidic in water because of the equilibrium

$$Al(H_2O)_6{}^{3+}(aq) + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$

The equilibrium, while not actually *strongly* favoring the products, does produce enough hydronium ion so that a 0.1 *M* solution of $AlCl_3$ in water has about the same concentration of hydronium ions as a 0.1 *M* solution of acetic acid, roughly 1×10^{-3} *M*.

Periodic Trends in the Acidity of Metal Ions

Within the periodic table, atomic size increases down a group and decreases from left to right in a period. Cation sizes follow these same trends, so within a given group, the cation of the metal at the top of the group has the smallest volume and the largest charge density. Therefore, hydrated metal ions at the top of a group in the periodic table are the most acidic within the group.

The cations of the Group 1A metals (Li^+, Na^+, K^+, Rb^+, and Cs^+), with charges of just 1+, have little tendency to increase the H_3O^+ concentration in an aqueous solution.

Within Group 2A, the Be^{2+} cation is very small and has sufficient charge density to cause the hydrated ion to be a weak acid. The other cations of Group 2A (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), have charge densities that become progressively smaller as we go down the group. Although their hydrated ions all generate some hydronium ion in water, the amount is negligible.

Some transition metal ions are also acidic, especially those with charges of 3+. For example, solutions containing salts of Fe^{3+} and Cr^{3+} tend to be acidic because their ions in solution exist as $Fe(H_2O)_6{}^{3+}$ and $Cr(H_2O)_6{}^{3+}$, respectively, and undergo the same ionization reaction as does the $Al(H_2O)_6{}^{3+}$ ion discussed previously.

Influence of Oxidation Number on the Acidity of Metal Oxides

Not all metal oxides are basic. As the oxidation number (or charge) on a metal ion increases, the metal ion becomes more *acidic*; it becomes a better electron pair acceptor. For metal hydrates, we've seen that this causes electron density to be pulled from the OH bonds of water molecules, causing the hydrate itself to become a weak proton donor. The increasing acidity of metal ions with increasing charge also affects the basicity of their oxides.

When the positive charge on a metal is small, the oxide tends to be basic, as we've seen for oxides such as Na_2O and CaO. With ions having a 3+ charge, the oxides are less basic and begin to take on acidic properties as well; they become amphoteric. (Recall from Section 16.1 that a substance is *amphoteric* if it is capable of reacting as either an acid or a base.) Aluminum oxide is an example; it can react with both acids and bases. It has basic properties when it dissolves in acid.

$$Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O$$

As noted earlier, the hydrated aluminum ion has six water molecules surrounding it, so in an acidic solution the aluminum exists primarily as $Al(H_2O)_6{}^{3+}$.

Aluminum oxide exhibits acidic properties when it dissolves in a base. One way to write the equation for the reaction is

$$\mathrm{Al_2O_3}(s) + 2\mathrm{OH^-}(aq) \longrightarrow 2\mathrm{AlO_2^-}(aq) + \mathrm{H_2O}$$

Actually, in basic solution the formula of the aluminum-containing species is more complex than this and is better approximated by $\mathrm{Al(H_2O)_2(OH)_4^-}$. Note that the difference between the two formulas is just the number of water molecules involved in the formation of the ion.

$$\mathrm{Al(H_2O)_2(OH)_4^-} \text{ is equivalent to } \mathrm{AlO_2^-} + 4\mathrm{H_2O}$$

However we write the formula for the aluminum-containing ion, it is an anion, not a cation.

When the metal is in a very high oxidation state, the oxide becomes acidic. Chromium(VI) oxide, CrO_3, is an example. When dissolved in water, the resulting solution is quite acidic and is called chromic acid. One of the principal species in the solution is H_2CrO_4, which is a strong acid that is more than 95% ionized. The acid forms salts containing the chromate ion, CrO_4^{2-}.

16.6 | Advanced Ceramics and Acid–Base Chemistry

Ceramic materials have a long history, dating to prehistoric times. Examples of pottery about 13,000 years old have been found in several parts of the world. Today, manufactured ceramics include common inorganic building materials such as brick, cement, and glass. We find ceramics around the home as porcelain dinnerware, tiles, sinks, toilets, and artistic pottery and figurines. These materials are made from inorganic minerals such as clay, silica (sand), and other silicates (compounds containing anions composed of silicon and oxygen), which are taken from the earth's crust.

In recent times, an entirely new set of materials, generally referred to as *advanced ceramics,* have been prepared by chemists in laboratories and have high-tech applications. We find such ceramics in places we wouldn't expect, such as in cell phones and inside diesel engines.

Several methods are used to form ceramics from their raw materials. In many cases, the components of the ceramic are first pulverized to give a very fine powder. The powder is then mixed with water to form a slurry that can be poured into a mold where it sets up into a solid form that has little structural strength. (Alternatively, the fine powder is mixed with a binder and pressed into the desired shape.) The newly formed object is next placed in a kiln where it is heated to a high temperature, often over 1000 °C. At these high temperatures the fine particles stick together by a process called **sintering**, which produces the finished ceramic. Although sintering is sometimes accompanied by partial melting of the fine particles, often the particles remain entirely solid during the process.

There are some problems with making ceramics by the traditional methods just described. Because it is difficult to produce uniform and very small particle sizes by grinding, ceramics made from materials prepared this way often contain small cracks and voids, which adversely affect physical properties such as strength. In addition, the chemical composition of the ceramic cannot be easily and reproducibly controlled by mixing various powdered components.

The Sol-Gel Process

For some types of ceramics, the problems of particle size and uniformity can be avoided by using a method called the **sol-gel process**. The chemistry involved is based on acid–base reactions similar to those discussed earlier in this chapter. The starting materials are metal salts or compounds in which a metal or metalloid (e.g., Si) is bonded to some number of

CHEMISTRY OUTSIDE THE CLASSROOM 16.1

Applications of Advanced Ceramic Materials

There are some properties that all ceramics have in common, and there are others that can be tailored by controlling the ceramic's composition and method of preparation. For example, virtually all ceramic materials have extremely high melting points and are much harder than steel. Some, such as boron nitride, BN, are nearly as hard as diamond, the hardest substance known. Silicon carbide, SiC, is a hard and relatively inexpensive ceramic to make in bulk and has long been used as an abrasive in sandpaper and grinding wheels.

The high strength and relatively low density of ceramic materials make them useful for applications in space. They are used to line the surfaces of rocket engines because they transmit heat very slowly and are able to protect the metals used to construct the engines from melting. The exterior of the space shuttle (Figure 1) is coated with protective ceramic tiles that serve as thermal "heat" shields during re-entry from space. The tiles are made of a low-density porous silica ceramic derived from common sand, SiO_2. They are able to withstand very high temperatures and have a very low thermal conductivity, preventing heat transfer to the body of the shuttle.

High-tech ceramics are relatively new materials, and new applications for them are continually being found. It is interesting to note how varied their uses are. Here are a few examples.

Thin ceramic films, deposited by the sol-gel process or other methods, are found on optical surfaces where they serve as antireflective coatings and as filters for lighting. Tools such as drill bits are given thin coatings of titanium nitride (TiN) to make them more wear resistant (Figure 2).

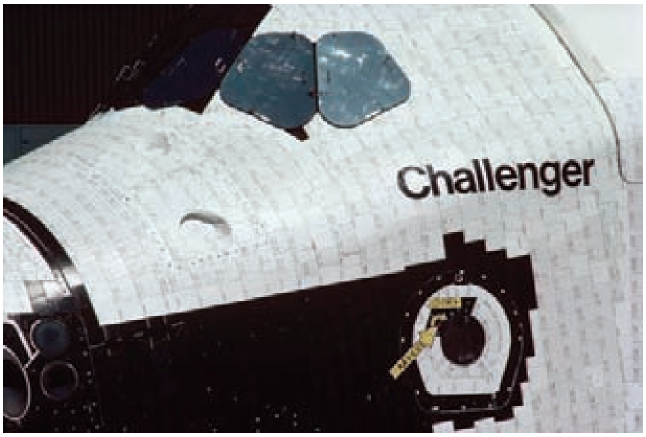


Figure 1 **Space shuttle heat shield.** Individual heat-shielding ceramic tiles are visible on the surface of the space shuttle *Challenger*. The photo was taken shortly after the spacecraft was completed. In 1986, the *Challenger* was lost in a tragic accident shortly after lift-off. Damage to the tiles during liftoff is believed to be responsible for the loss of the *Columbia* and its crew in February 2003 when the spacecraft broke apart during reentry into the earth's atmosphere. *(Roger Ressmeyer/© Corbis)*

Figure 2 **Titanium nitride.** A drill bit with a thin golden coating of titanium nitride, TiN, will retain its sharpness longer than steel drill bits. *(Andy Washnik)*

Zirconia (ZrO_2) is used to make ceramic golf spikes for golf shoes, as well as portions of hip-joint replacement parts for medicine and knives that stay sharp much longer than steel. All these applications are possible because of the hardness of the ZrO_2 ceramic.

Boron nitride (BN) powder is composed of flat, plate-like crystals that can easily slide over one another, and one of its uses is in cosmetics, where it gives a silky texture to the product (Figure 3). Another boron-containing ceramic, boron carbide, is used along with Kevlar polymer to make bulletproof vests. When a bullet strikes the vest, it is shattered by the ceramic, which absorbs most of the kinetic energy, with residual energy being absorbed by the Kevlar backing.

Silicon nitride, Si_3N_4, is used to make engine components for diesel engines because it is extremely hard and wear resistant, has a high stiffness with low density, and can withstand extremely high temperatures and harsh chemical environments.

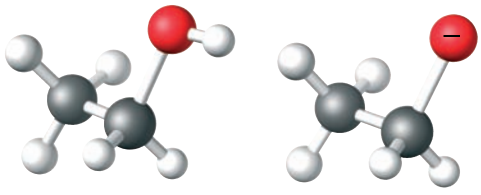
Piezoelectric ceramics have the property that they produce an electric potential when their shape is deformed. Conversely, they deform when an electric potential is applied to them. A company makes "smart skis" that incorporate piezoelectric devices that use both properties. Vibrations in the skis are detected by the potential developed when they deform. A potential is then applied to cancel the vibration. This "smart materials" technology was first developed to dampen vibrations in optical components of the "Star Wars" weapons system designed to protect the United States from missile attack.

ALMAY
Skin Stays Clean
REVLON
AGE DEFYING
WET/DRY
ALMAY
REVLON
AGE DEFYING

Figure 3 **Ceramics in cosmetics.** A variety of cosmetics use boron nitride, BN, as an ingredient. *(Andy Washnik)*

alkoxide groups. An *alkoxide* is an anion formed by removing a hydrogen ion from an alcohol.[6] For instance, removal of H^+ from ethanol yields the ethoxide ion.

$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow{-H^+} \underset{\text{ethoxide ion}}{C_2H_5O^-}$$



The ethoxide ion forms salts with metal ions that generally are soluble in ethanol, which should not be surprising considering the similarities between the solute and solvent.

Alcohols are extremely weak acids with very little tendency to lose H^+ ions, so alkoxide ions are very strong bases with a *very strong* affinity for H^+. When placed in water they react immediately and completely by removing H^+ from H_2O to give the alcohol and hydroxide ion.

$$C_2H_5O^- + H_2O \xrightarrow{100\%} C_2H_5OH + OH^-$$

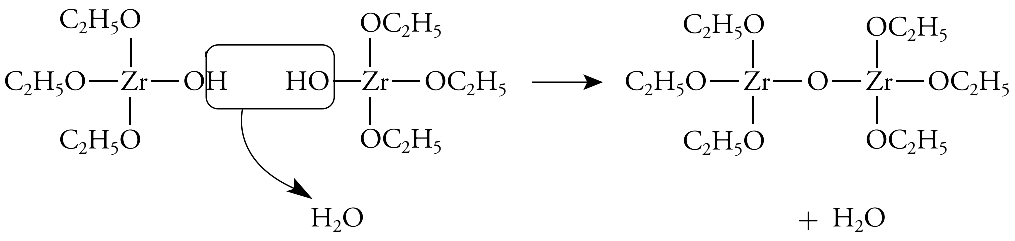
This reaction forms the basis for the start of a sequence of reactions that ultimately yields the ceramic material. Let's use zirconium(IV) ethoxide, $Zr(C_2H_5O)_4$, to illustrate the process.

■ Typical metals used in the sol-gel process are Si, Ti, Zr, Al, Sn, and Ce, all with high oxidation states.

The sequence of reactions begins with the gradual addition of water to an alcohol solution of $Zr(C_2H_5O)_4$, which causes ethoxide ions to react to form ethanol and be replaced by hydroxide ions. This reaction is called **hydrolysis** because it involves a reaction with water. The first step in the process is

$$Zr(C_2H_5O)_4 + H_2O \longrightarrow Zr(C_2H_5O)_3OH + C_2H_5OH$$

The large positive charge on the zirconium ion binds the OH^- tightly and polarizes the O—H bond, causing it to weaken. When two $Zr(C_2H_5O)_3OH$ units encounter each other they undergo an acid–base reaction. A proton is transferred from the OH attached to one zirconium ion to the OH attached to another zirconium ion. The result is the simultaneous formation of a water molecule and an oxygen bridge between the two zirconium ions.



$$\underset{C_2H_5O}{\overset{C_2H_5O}{C_2H_5O-Zr-}}\boxed{OH \quad HO}\underset{OC_2H_5}{\overset{OC_2H_5}{-Zr-OC_2H_5}} \longrightarrow \underset{C_2H_5O}{\overset{C_2H_5O}{C_2H_5O-Zr-}}O\underset{OC_2H_5}{\overset{OC_2H_5}{-Zr-OC_2H_5}} + H_2O$$

$$H_2O$$

As more and more water is added, this process continues, with ethoxide ions changing to ethanol molecules and more and more oxygen bridges being formed between zirconium ions. The result is a network of zirconium atoms bridged by oxygens, which produces extremely small insoluble particles that are essentially oxides with many residual hydroxide ions. These particles are suspended in the alcohol solvent and have a gel-like quality.[7]

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[6] An **alkyl** group is a hydrocarbon fragment derived from an alkane by removal of a hydrogen atom. For example, the methyl group, CH_3—, is derived from methane, CH_4, and is an alkyl group. If we represent an alcohol by the general formula R—OH, where R represents an alkyl group, then the general formula of an alkoxide ion is $R—O^-$.

[7] The particle size is larger than one would find in a true solution, but smaller than in a typical precipitate. This type of mixture is called a *colloid*, and a colloid composed of tiny solid particles suspended in a liquid medium is called a *sol*. That's where part of the name *sol-gel* comes from.

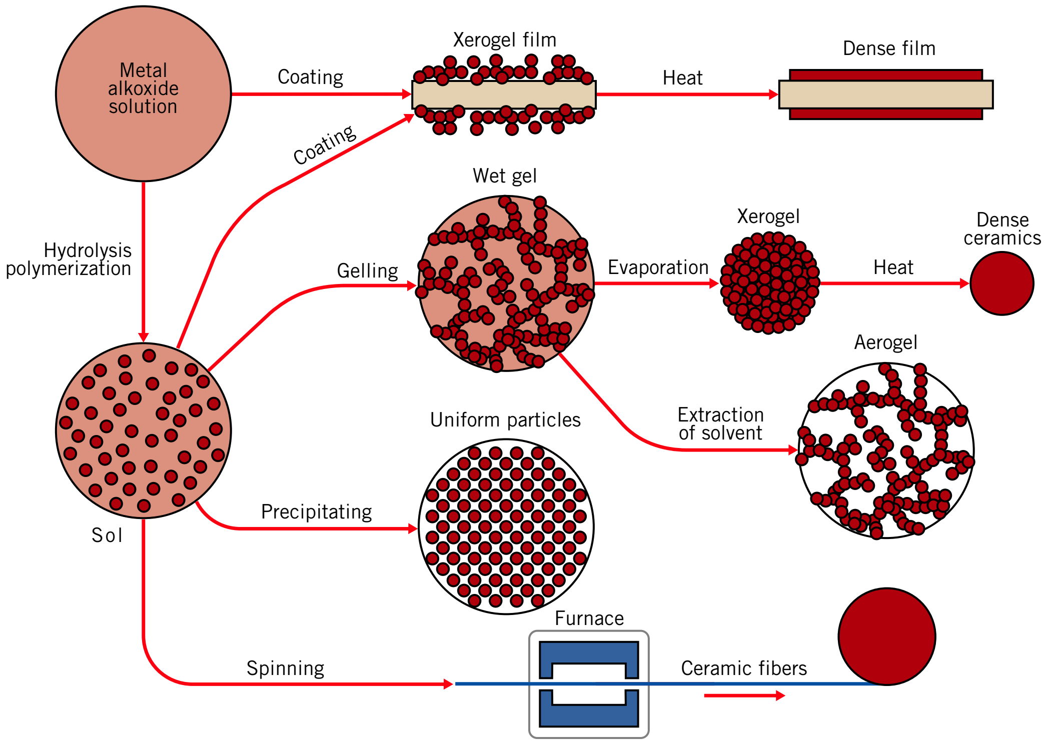


Figure 16.5 | **Sol-gel technologies and their products.**

Once the sol-gel suspension is formed, it can be used in a number of ways, as indicated in Figure 16.5. It can be deposited on a surface by dip coating to yield very thin ceramic coatings. It can be cast into a mold to produce a semisolid gelatin-like material (wet gel). The wet gel can be dried by evaporation of the solvent to give a porous solid called a **xerogel.** Further heating causes the porous structure of the xerogel to collapse and form a dense ceramic or glass with a uniform structure. If the solvent is removed from the wet gel under supercritical conditions (at a temperature above the critical temperature of the solvent), a very porous and extremely low density solid called an **aerogel** is formed (see the photo on page 61). By adjusting the viscosity of the gel suspension, ceramic fibers can be formed. And by precipitation, ultrafine and uniform ceramic powders are formed. What is amazing is that all these different forms can be made from the same material depending on how the suspension is handled.

■ Xerogels have very large internal surface areas because of their fine porous structure. Some have been found to be useful catalysts.

Summary

Brønsted–Lowry Acids and Bases. A **Brønsted–Lowry acid** (often simply referred to as a **Brønsted acid**) is a proton donor; a **Brønsted–Lowry base** (or simply **Brønsted base**) is a proton acceptor. According to the Brønsted–Lowry approach, an acid–base reaction is a proton transfer event. In an equilibrium involving a Brønsted acid and base, there are two **conjugate acid–base pairs.** The members of any given acid–base pair differ from each other by only one H^+, with the acid having one more H^+ than the base. A substance that can be either an acid or a base, depending on the nature of the other reactant, is **amphoteric** or, with emphasis on proton–transfer reactions, **amphiprotic**.

Lewis Acids and Bases. A **Lewis acid** accepts a pair of electrons from a **Lewis base** in the formation of a coordinate covalent bond. Lewis bases often have filled valence shells and must have at least one unshared electron pair. Lewis acids have an incomplete valence shell that can accept an electron pair, have double bonds that allow electron pairs to be moved to make room for an incoming electron pair from a Lewis base, or have valence shells that can accept more than an octet of electrons.

Relative Acidities and the Periodic Table. **Binary acids** contain only hydrogen and another nonmetal. Their strengths increase from top to bottom within a group and left to right across a period. **Oxoacids**, which contain oxygen atoms in addition to hydrogen and another element, increase in strength as the number of oxygen atoms on the same central atom increases. Delocalization of negative charge enhances the stability of oxoacid anions, making them weaker bases and, as a result, their conjugate acids are correspondingly stronger. Oxoacids having the same number of oxygens generally increase in strength as the central atom moves from bottom to top within a group and from left to right across a period.

Acid–Base Properties of the Elements and Their Oxides. Oxides of metals are basic anhydrides when the charge on the ion is small. Those of the Groups 1A and 2A metals neutralize acids and tend to react with water to form soluble metal hydroxides. The hydrates of metal ions tend to be proton donors when the positive charge density of the metal ion is itself sufficiently high, as it is when the ion has a 3+ charge. The small beryllium ion, Be^{2+}, forms a weakly acidic hydrated ion. Metal oxides become more acidic as the oxidation number of the metal becomes larger. Aluminum oxide is amphoteric, dissolving in both acids and bases. Chromium(VI) oxide is acidic, forming chromic acid when it dissolves in water.

Advanced Ceramics. Common ceramic materials are made from inorganic minerals obtained from the earth's crust. They are ground to fine powders, formed into shapes, and fired at high temperatures where **sintering** occurs, causing the fine particles to stick together to give a rigid solid. The **sol-gel process** uses the reaction of water with metal **alkoxides** to form extremely small, gel-like particles suspended in alcohol that can be used in a variety of ways to give coatings, **xerogels, aerogels**, fibers, and ultrafine powders for making ceramics.

Tools for Problem Solving

The following tools related to acid–base reactions were introduced in this chapter.

Brønsted–Lowry definitions (page 742)
The Brønsted–Lowry acid–base definitions, acids are proton donors and bases are proton acceptors, are useful to keep in mind whenever working with acids and bases, especially in aqueous solutions.

Conjugate acid–base pairs (page 743)
Every conjugate acid–base pair consists of an acid plus a base with less proton (H^+). You should be able to write the formula of a conjugate acid, given the formula of the base, and vice versa.

Conjugate acid–base equilibria (page 744)
The conjugate acid is always on the opposite side of an equation from its conjugate base, and the Brønsted–Lowry acid–base equilibrium is typically written with two sets of conjugate acid–base pairs.

Acid–base strength and the position of equilibrium (page 748)
If you know the relative strengths of the acids or bases in an equilibrium, you can predict the position of equilibrium. You can also use the position of equilibrium to establish the relative strengths of the acids or bases in an equilibrium.

Reciprocal relationship in acid–base strengths (page 748)
The stronger an acid, the weaker is its conjugate base. This tool can help establish the position of equilibrium when dealing with more than one acid–base pair.

Periodic trends in strengths of binary acids (page 750)
The acidities of $H—X$ bonds increases from left to right across a period and from top to bottom in a group. You can use the trends to predict the relative acidities of $X—H$ bonds, both for the binary hydrides themselves and for molecules that contain $X—H$ bonds.

Trends in the strengths of oxoacids (pages 750 and 753)
You use the trends to predict the relative acidities of oxoacids according to the nature of the central nonmetal as well as the number of oxygens attached to a given nonmetal. The principles involved also let you compare acidities of compounds containing different electronegative elements or electron-attracting groups bonded to an atom bonded to an —OH group.

Lewis acid–base definitions (page 755)
Keep the definitions in mind whenever analyzing an acid–base reaction in terms of Lewis acids and bases.

Acidity of metal cations (page 760)
Metal ions become better at polarizing H_2O molecules as their charge increases and their size decreases. Use this to compare the relative abilities of different metal ions to produce acidic solutions in water.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Brønsted–Lowry Acids and Bases

16.1 How is a Brønsted acid defined? How is a Brønsted base defined?

16.2 How are the formulas of the members of a conjugate acid–base pair related to each other? Within the pair, how can you tell which is the acid?

16.3 Is H_2SO_4 the conjugate acid of SO_4^{2-}? Explain your answer.

16.4 What is meant by the term *amphoteric*? Give two chemical equations that illustrate the amphoteric nature of water.

16.5 Define the term amphiprotic.

Trends in Acid–Base Strengths

16.6 Within the periodic table, how do the strengths of the binary acids vary from left to right across a period? How do they vary from top to bottom within a group?

16.7 Astatine, atomic number 85, is radioactive and does not occur in appreciable amounts in nature. On the basis of what you have learned in this chapter, answer the following.

(a) How would the acid strength of HAt compare with that of HI?

(b) How would the acid strength of $HAtO_3$ compare with that of $HBrO_3$?

16.8 Explain why nitric acid is a stronger acid than nitrous acid.

$HO—NO_2$	$HO—NO$
nitric acid	nitrous acid

16.9 Explain why H_2S is a stronger acid than H_2O.

16.10 Which is the stronger Brønsted–Lowry base, $CH_3CH_2O^-$ or $CH_3CH_2S^-$? What is the basis for your selection?

16.11 Explain why $HClO_4$ is a stronger acid than H_2SeO_4.

16.12 The position of equilibrium in the equation below lies far to the left. Identify the conjugate acid–base pairs. Which of the two acids is stronger?

$$HOCl(aq) + H_2O \rightleftharpoons H_3O^+(aq) + OCl^-(aq)$$

16.13 Consider the following: CO_3^{2-} is a weaker base than hydroxide ion, and HCO_3^- is a stronger acid than water. In the equation below, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

16.14 Acetic acid, $HC_2H_3O_2$, is a weaker acid than nitrous acid, HNO_2. How do the strengths of the bases $C_2H_3O_2^-$ and NO_2^- compare?

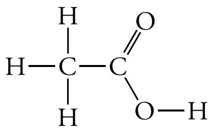
16.15 Nitric acid, HNO_3, is a very strong acid. It is 100% ionized in water. In the reaction below, would the position of equilibrium lie to the left or to the right?

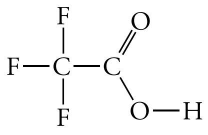
$$NO_3^-(aq) + H_2O \rightleftharpoons HNO_3(aq) + OH^-(aq)$$

16.16 $HClO_4$ is a stronger proton donor than HNO_3, but in water both acids appear to be of equal strength; they are both 100% ionized. Why is this so? What solvent property would be necessary in order to distinguish between the acidities of these two Brønsted–Lowry acids?

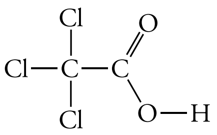
16.17 Formic acid, $HCHO_2$, and acetic acid, $HC_2H_3O_2$, are classified as weak acids, but in water $HCHO_2$ is more fully ionized than $HC_2H_3O_2$. However, if we use liquid ammonia as a solvent for these acids, they both appear to be of equal strengths; both are 100% ionized in liquid ammonia. Explain why this is so.

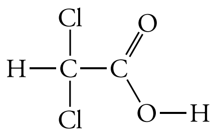
16.18 Which of the molecules below is expected to be the stronger Brønsted–Lowry acid? Why?





16.19 Which of the molecules below has the stronger conjugate base? Explain your choice.



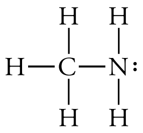


Lewis Acids and Bases

16.20 Define Lewis acid and Lewis base.

16.21 Explain why the addition of a proton to a water molecule to give H_3O^+ is a Lewis acid–base reaction.

16.22 Methylamine has the formula CH_3NH_2 and the structure



$$\begin{array}{ccccc} & & H & & H \\ & & | & & | \\ H & — & C & — & N\!: \\ & & | & & | \\ & & H & & H \end{array}$$

Use Lewis structures to illustrate the reaction of methylamine with boron trifluoride.

16.23 Use Lewis structures to show the Lewis acid–base reaction between SO_3 and H_2O to give H_2SO_4. Identify the Lewis acid and the Lewis base in the reaction.

16.24 Explain why the oxide ion, O^{2-}, can function as a Lewis base but not as a Lewis acid.

16.25 The molecule SbF_5 is able to function as a Lewis acid. Explain why it is able to be a Lewis acid.

16.26 In the reaction of calcium with oxygen to form calcium oxide, each calcium gives a pair of electrons to an oxygen atom. Why isn't this viewed as a Lewis acid–base reaction?

Acid–Base Properties of the Elements and Their Oxides

16.27 Suppose that a new element was discovered. Based on the discussions in this chapter, what properties (both physical and chemical) might be used to classify the element as a metal or a nonmetal?

16.28 If the oxide of an element dissolves in water to give an acidic solution, is the element more likely to be a metal or a nonmetal?

16.29 Boric acid is very poisonous and is used in ant bait (to kill ant colonies) and to poison cockroaches. It is a weak acid with a formula often written as H_3BO_3, although it is better written as $B(OH)_3$. It functions not as a Brønsted–Lowry acid, but as a Lewis acid. Using Lewis structures, show how $B(OH)_3$ can bind to a water molecule and cause the resulting product to be a weak Brønsted acid.

16.30 Many chromium salts crystallize as hydrates containing the ion $Cr(H_2O)_6^{3+}$. Solutions of these salts tend to be acidic. Explain why.

16.31 Which ion is expected to give the more acidic solution, Fe^{2+} or Fe^{3+}? Why?

16.32 Ions of the alkali metals have little effect on the acidity of a solution. Why?

16.33 What acid is formed when the following oxides react with water?

(a) SO_3

(b) CO_2

(c) P_4O_{10}

16.34 Consider the following oxides: CrO, Cr_2O_3, CrO_3.

(a) Which is most acidic?

(b) Which is most basic?

(c) Which is most likely to be amphoteric?

16.35 Write equations for the reaction of Al_2O_3 with

(a) a strong acid, and

(b) a strong base.

Review Problems

Brønsted Acids and Bases

OH **16.36** Write the formula for the conjugate acid of each of the following.

(a) F^- **(c)** C_5H_5N **(e)** $HCrO_4^-$

(b) N_2H_4 **(d)** O_2^{2-}

16.37 Write the formula for the conjugate base of each of the following.

(a) NH_2OH **(c)** HCN **(e)** HNO_2

(b) HSO_3^- **(d)** H_5IO_6

16.38 Identify the conjugate acid–base pairs in the following reactions.

(a) $HNO_3 + N_2H_4 \rightleftharpoons NO_3^- + N_2H_5^+$

(b) $NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$

(c) $H_2PO_4^- + CO_3^{2-} \rightleftharpoons HPO_4^{2-} + HCO_3^-$

(d) $HIO_3 + HC_2O_4^- \rightleftharpoons IO_3^- + H_2C_2O_4$

16.39 Identify the conjugate acid–base pairs in the following reactions.

(a) $HSO_4^- + SO_3^{2-} \rightleftharpoons HSO_3^- + SO_4^{2-}$

(b) $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$

(c) $CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$

(d) $H_2Se + H_2O \rightleftharpoons HSe^- + H_3O^+$

Trends in Acid–Base Strengths

16.40 Choose the stronger acid: **(a)** HBr or HCl; **(b)** H_2O or HF; **(c)** H_2S or HBr. Give your reasons.

16.41 Choose the stronger acid: **(a)** H_2S or H_2Se; **(b)** H_2Te or HI; **(c)** PH_3 or NH_3. Give your reasons.

16.42 Choose the stronger acid and give your reason:

(a) HOCl or $HClO_2$;

(b) H_2SeO_4 or H_2SeO_3.

16.43 Choose the stronger acid: **(a)** HIO_3 or HIO_4; **(b)** H_3AsO_4 or H_3AsO_3. Give your reasons.

OH **16.44** Choose the stronger acid: **(a)** $HClO_3$ or HIO_3; **(b)** HIO_2 or $HClO_3$; **(c)** H_2SeO_3 or $HBrO_4$. Give your reasons.

16.45 Choose the stronger acid: **(a)** H_3AsO_4 or H_3PO_4; **(b)** H_2CO_3 or HNO_3; **(c)** H_2SeO_4 or $HClO_4$. Give your reasons.

Acidity of Metal Oxides and Hydrated Metal Ions

16.46 The ion $Cr(H_2O)_6^{3+}$ is weakly acidic. Write an equation showing its behavior as a Brønsted–Lowry acid in water.

16.47 The compound $Mg(OH)_2$ is basic, but $Si(OH)_4$ is an acid (silicic acid). Why?

Lewis Acids and Bases

16.48 Use Lewis symbols to diagram the reaction

$$NH_2^- + H^+ \longrightarrow NH_3$$

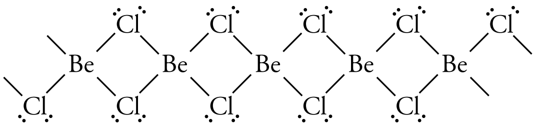
Identify the Lewis acid and Lewis base in the reaction.

16.49 Use Lewis symbols to diagram the reaction

$$BF_3 + F^- \longrightarrow BF_4^-$$

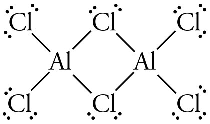
Identify the Lewis acid and Lewis base in the reaction.

16.50 Beryllium chloride, $BeCl_2$, exists in the solid as a polymer composed of long chains of $BeCl_2$ units arranged as follows.



The formula of the chain can be represented as $(BeCl_2)_n$, where n is a large number. Use Lewis structures to show how the reaction $nBeCl_2 \longrightarrow (BeCl_2)_n$ is a Lewis acid–base reaction.

16.51 Aluminum chloride, $AlCl_3$, forms molecules with itself with the formula Al_2Cl_6. Its structure is



Use Lewis structures to show how the reaction $2AlCl_3 \longrightarrow Al_2Cl_6$ is a Lewis acid–base reaction.

OH **16.52** Use Lewis structures to diagram the reaction

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Identify the Lewis acid and Lewis base in this reaction.

16.53 Use Lewis structures to diagram the reaction

$$CO_2 + O^{2-} \longrightarrow CO_3^{2-}$$

Identify the Lewis acid and Lewis base in this reaction.

16.54 Use Lewis structures to show how the following reaction can be viewed as the displacement of one Lewis base by another Lewis base from a Lewis acid. Identify the two Lewis bases and the Lewis acid.

$$NH_2^- + H_2O \longrightarrow NH_3 + OH^-$$

OH **16.55** Use Lewis structures to show how the following reaction involves the transfer of a Lewis base from one Lewis acid to another. Identify the two Lewis acids and the Lewis base.

$$CO_3^{2-} + SO_2 \longrightarrow CO_2 + SO_3^{2-}$$

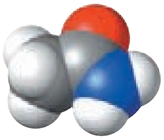
Additional Exercises

16.56 What is the formula of the conjugate acid of dimethylamine, $(CH_3)_2NH$? What is the formula of its conjugate base?

***16.57** Using liquid ammonia as a solvent, sodium amide reacts with ammonium chloride in an acid–base neutralization reaction. Assuming that these compounds are completely dissociated in liquid ammonia, write molecular, ionic, and net ionic equations for the reaction. Which substance is the acid and which is the base?

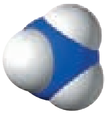
***16.58** In liquid SO_2 as a solvent, $SOCl_2$ reacts with Na_2SO_3 in a reaction that can be classified as neutralization (acid plus base yields solvent plus a salt). Write an equation for the reaction. Which solute is the acid and which is the base? Describe what is happening in terms of the Lewis definition of acids and bases.

16.59 The following space-filling model depicts the structure of a compound called ethanamide.

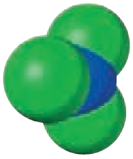


How would you expect its base strength to compare with that of ammonia? Justify your answer.

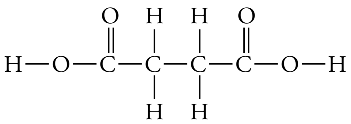
16.60 Which of the following compounds is the stronger base? Explain.



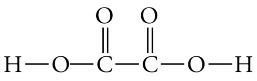
or



16.61 Which of the two molecules below is the stronger Brønsted–Lowry acid? Why?



$$\mathrm{HO{-}C({=}O){-}CH_2{-}CH_2{-}C({=}O){-}OH}$$



$$\mathrm{HO{-}C({=}O){-}C({=}O){-}OH}$$

16.62 Write equations that illustrate the amphiprotic nature of the bicarbonate ion.

16.63 Hydrogen peroxide is a stronger Brønsted–Lowry acid than water.

(a) Explain why this is so.

(b) Is an aqueous solution of hydrogen peroxide acidic or basic?

16.64 Sodium hydroxide, NaOH, is basic. Aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is amphoteric. The compound O_3ClOH (usually written $HClO_4$) is acidic. Considering that each compound contains one or more OH groups, why are their acid–base properties so different?

16.65 Hydrazine, N_2H_4, is a weaker Brønsted–Lowry base than ammonia. In the following reaction, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$N_2H_5^+ + NH_3 \rightleftharpoons N_2H_4 + NH_4^+$$

16.66 Identify the two Brønsted–Lowry acids and two bases in the reaction

$$NH_2OH + CH_3NH_3^+ \rightleftharpoons NH_3OH^+ + CH_3NH_2$$

16.67 In the reaction in the preceding exercise, the position of equilibrium lies to left. Identify the stronger acid in each of the conjugate pairs in the reaction.

***16.68** How would you expect the degree of ionization of $HClO_3$ to compare in the solvents $H_2O(l)$ and $HF(l)$? The reactions are

$$HClO_3 + H_2O \rightleftharpoons H_3O^+ + ClO_3^-$$
$$HClO_3 + HF \rightleftharpoons H_2F^+ + ClO_3^-$$

Justify your answer.

Multi-Concept Problems

***16.69** On the basis of the VSEPR theory, sketch the structure of the $Al(H_2O)_6^{3+}$ ion. Sketch the two possible structures of the ion formed when a proton is removed from four of the six water molecules. Which is the more likely of the two structures?

16.70 A mixture is prepared containing 0.10 *M* of each of the following: arsenic acid, sodium arsenate, arsenous acid, and sodium arsenite. What are the formulas and chemical structures of the predominant arsenic-containing species present in the solution at equilibrium? Write the equation for the equilibrium.

Exercises in Critical Thinking

16.71 Are all Arrhenius acids Brønsted–Lowry acids? Are they all Lewis acids? Give examples if they are not. Give a reasoned explanation if they are.

16.72 How could you determine whether HBr is a stronger acid than HI?

16.73 Alcohols are organic compounds that have an —OH group. Are alcohols acids or bases? Sugars have an —OH group on almost every carbon atom; are they acids or bases? Phenol is a benzene ring with an —OH group. Is phenol an acid or base?

16.74 Acid rain, acid mine runoff, and acid leaching of metals from soils are important environmental considerations. What do these topics refer to and how do they affect you as a person?

Chapters 14–16

Bringing It Together

Again we pause to provide you with an opportunity to see how well you have grasped concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–13. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. At 25 °C and $[OH^-] = 1.00\ M$, the reaction

$$I^-(aq) + OCl^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

has the rate law: rate $= (0.60\ \text{L mol}^{-1}\ \text{s}^{-1})[I^-][OCl^-]$. Calculate the rates of the reaction when $[OH^-] = 1.00\ M$ in solutions with the following compositions:

(a) 0.74 g KI dissolved in 475 mL of a solution that contains $0.0200\ M\ OCl^-$.

(b) $[I^-] = 0.100\ M$ and $[OCl^-] = 0.0400\ M$.

2. A reaction has the stoichiometry: $3A + B \longrightarrow C + D$. The following data were obtained for the initial rate of formation of C at various concentrations of A and B.

Initial Concentrations		Initial Rate of Formation of C (mol L^{-1} s^{-1})
[A]	**[B]**	
0.010	0.010	2.0×10^{-4}
0.020	0.010	8.0×10^{-4}
0.020	0.033	2.64×10^{-3}

(a) What is the rate law for the reaction?

(b) What is the value of the rate constant?

(c) What is the rate at which C is formed if $[A] = 0.017\ M$ and $[B] = 0.033\ M$?

3. If the concentration of a particular reactant is doubled and the rate of the reaction is cut in half, what must be the order of the reaction with respect to that reactant?

4. Organic compounds that contain large proportions of nitrogen and oxygen tend to be unstable and are easily decomposed. Hexanitroethane, $C_2(NO_2)_6$, decomposes according to the equation

$$C_2(NO_2)_6 \longrightarrow 2NO_2 + 4NO + 2CO_2$$

The reaction in CCl_4 as a solvent is first-order with respect to $C_2(NO_2)_6$. At 70.0 °C, $k = 2.41 \times 10^{-6}\ s^{-1}$ and at 100.0 °C $k = 2.22 \times 10^{-4}\ s^{-1}$.

(a) What is the half-life of $C_2(NO_2)_6$ at 70.0 °C? What is the half-life at 100.0 °C?

(b) If 2.24 g of $C_2(NO_2)_6$ is dissolved in CCl_4 at 70.0 °C to give 125 mL of solution, what will be the $C_2(NO_2)_6$ concentration after 525 minutes?

(c) What is the value of the activation energy of this reaction, expressed in kilojoules?

(d) What is the reaction's rate constant at 120.0 °C?

(e) Draw a reasonable Lewis structure for $C_2(NO_2)_6$.

5. Radioactive strontium-90, ^{90}Sr, has a half-life of 28 years.

(a) What fraction of a sample of ^{90}Sr will remain after three half-lives?

(b) What fraction of a sample of ^{90}Sr will remain after 168 years?

(c) If the amount of ^{90}Sr remaining in a sample is only one-sixteenth of the amount originally present, how many years has the sample been undergoing radioactive decay?

(d) If the amount of ^{90}Sr remaining in a sample is only one-sixth of the amount originally present, how many years has the sample been undergoing radioactive decay?

6. The reaction $2A + 2B \longrightarrow M + N$ has the rate law: rate $= k[A]^2$. At 25 °C, $k = 1.0 \times 10^{-4}$ L mol^{-1} s^{-1}. If the initial concentrations of A and B are $0.250\ M$ and $0.150\ M$, respectively.

(a) What is the half-life of the reaction?

(b) What will be the concentrations of A and B after 30.0 minutes?

7. The decomposition of ozone, O_3, is believed to occur by the two-step mechanism

$$\begin{array}{lr} O_3 \longrightarrow O_2 + O & \text{(slow)} \\ O + O_3 \longrightarrow 2O_2 & \text{(fast)} \\ \hline 2O_3 \longrightarrow 3O_2 & \text{(net reaction)} \end{array}$$

If this is the mechanism, what is the reaction's rate law?

8. One possible mechanism for the decomposition of ethane, C_2H_6, into ethylene, C_2H_4, and hydrogen,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

includes the following steps.

(1) $C_2H_6 \longrightarrow 2CH_3\cdot$
(2) $CH_3\cdot + C_2H_6 \longrightarrow CH_4 + C_2H_5\cdot$
(3) $C_2H_5\cdot \longrightarrow C_2H_4 + H\cdot$
(4) $H\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + H_2$
(5) $H\cdot + C_2H_5\cdot \longrightarrow C_2H_6$

(a) Which steps initiate the reaction?

(b) Which are propagation steps?

(c) Which is a termination step?

9. Write the appropriate mass-action expression, using molar concentrations, for these reactions.

(a) $NO_2(g) + N_2O(g) \rightleftharpoons 3NO(g)$

(b) $CaSO_3(s) \rightleftharpoons CaO(s) + SO_2(g)$

(c) $NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$

10. At a certain temperature, the reaction $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ has $K_c = 1.2 \times 10^{-13}$. Does this reaction proceed far toward completion when equilibrium is reached? If 0.010 mol HF was placed in a 1.00 L container and the system was permitted to come to equilibrium, what would be the concentrations of H_2 and F_2 in the container?

11. Suppose a mixture was prepared containing 0.0100 mol H_2, 0.0150 mol F_2, and 0.0180 mol HF in a 1.25 L reaction vessel. What will the concentrations of all the gases be when equilibrium is reached? The reaction is $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ for which the equilibrium constant $K_c = 1.2 \times 10^{-13}$.

12. At 100.0 °C, the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $K_P = 6.5 \times 10^{-2}$. What is the value of K_c at this temperature?

13. At 1000 °C, the reaction $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ has $K_c = 3.60$. If 0.100 mol NO_2 and 0.100 mol SO_2 are placed in a 5.00 L container and allowed to react, what will all the concentrations be when equilibrium is reached? What will the new equilibrium concentrations be if 0.010 mol NO and 0.010 mol SO_3 are added to this original equilibrium mixture?

14. At a certain temperature, $K_c = 0.450$ for the reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Suppose 7.0 g PCl_3 and 4.50 g Cl_2 are placed in a 12.0 L reaction vessel and allowed to come to equilibrium. How much heat in kilojoules will be absorbed or evolved by the time equilibrium has been reached? (Assume ΔH is effectively independent of temperature.)

15. For the reaction in the preceding question, $\Delta H° = -41.8$ kJ. How will the equilibrium concentration of NO be affected if:

(a) More NO_2 is added to the container?

(b) Some SO_3 is removed from the container?

(c) The temperature of the reaction mixture is raised?

(d) Some SO_2 is removed from the mixture?

(e) The pressure of the gas mixture is lowered by expanding the volume to 10.0 L?

16. At 100 °C, the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $K_P = 6.5 \times 10^{-2}$. Suppose a mixture of these gases was prepared at 100 °C in a 400 mL vessel with the following partial pressures: $P_{NO_2} = 0.348$ atm and $P_{N_2O_4} = 0.678$ atm. What will the partial pressures of the gases be at equilibrium? What will the total pressure of the gas mixture be? What is the total mass of gas in the reaction vessel?

17. Which is the stronger acid, H_3PO_3 or H_3PO_4? Justify your answer.

18. Which is the stronger acid, H_2S or H_2Te?

19. What are the conjugate acids of (a) HSO_3^-, (b) N_2H_4?

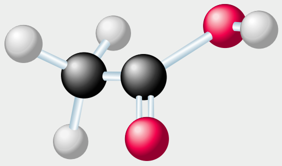
20. What are the conjugate bases of (a) HSO_3^-, (b) N_2H_4, (c) $C_5H_5NH^+$?

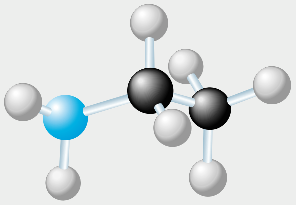
21. Identify the conjugate acid-base pairs in the reaction

$$CH_3NH_2 + NH_4^+ \rightleftharpoons CH_3NH_3^+ + NH_3$$

22. Methylamine, CH_3NH_2, is a weak base. Write the chemical equation for the equilibrium that occurs in an aqueous solution of this solute. Identify the two acids and two bases in the system.

23. Suppose the following two pure substances are mixed. Write the formulas of the ions that form. Which of the reactants is an acid and which is a base? Which of the ions that form is an acid and which is a base? Write the chemical equation for the reaction.



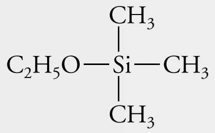


24. Use Lewis structures to diagram the reaction between the Lewis base OH^- and the Lewis acid SO_3.

25. *X*, *Y*, and *Z* are all nonmetallic elements in the same period of the periodic table where they occur, left to right, in the order given. Which would be a stronger binary acid than the binary acid of *Y*: the binary acid of *X* or the binary acid of *Z*? Explain.

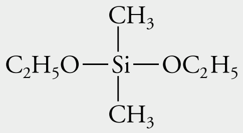
26. Is the compound $Sb(OH)_5$ likely to be acidic, basic, or neutral in water? Justify your answer.

27. Consider the two compounds shown below.



$$C_2H_5O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

(1)



$$C_2H_5O-\underset{CH_3}{\overset{CH_3}{Si}}-OC_2H_5$$

(2)

(a) Suppose water were added gradually to an ethanol solution of compound (1). Draw the Lewis structure of the product that would form.

(b) Use Lewis structures to describe the product that would form if an excess of water were added to an ethanol solution of compound (2).

28. If sodium metal is added to pure ethanol, the following reaction takes place in which sodium ethoxide (containing the strong Brønsted–Lowry base $C_2H_5O^-$) is formed.

$$2Na + 2C_2H_5OH \longrightarrow 2NaC_2H_5O + H_2(g)$$

Is this an acid base reaction? Explain.

29. The acetate ion is a weak Brønsted–Lowry base. Write a chemical equation that shows why an aqueous solution of sodium acetate is slightly basic.

17

Acid–Base Equilibria in Aqueous Solutions

Chapter Outline

17.1 | Water, pH, and "p" Notation

17.2 | pH of Strong Acid and Base Solutions

17.3 | Ionization Constants, K_a and K_b

17.4 | Determining K_a and K_b Values

17.5 | pH of Weak Acid and Weak Base Solutions

17.6 | pH of Salt Solutions

17.7 | Buffer Solutions

17.8 | Polyprotic Acids

17.9 | Acid–Base Titrations

This olympic weightlifter is using large amounts of energy to try to lift the heaviest weight in his event. Inside his body there are literally thousands of chemical reactions happen simultaneously in support of his effort. Some chemical reactions happen spontaneously without conscious thought. Other chemical reactions, such as those that cause muscle movement, occur in response to signals from the brain. Many of these reactions produce or consume acids and bases. The pain that the weightlifter will feel after his event may be from the buildup of lactic acid that occurs during strenuous exercise. Carbon dioxide, transported as the bicarbonate ion in the body, is another product of metabolism. Understanding how the body manages its acid–base balance starts with the fundamentals of acid–base equilibria. © AP/Wide World Photos.

This Chapter in Context

In Chapters 15 and 16 we discussed the general principles of chemical equilibrium and our concepts about the chemical properties of acids and bases. Using the principles from Chapter 10 about molecular polarity and the concept of delocalization of electrons, we were able to qualitatively compare the strengths of acids and bases. Our goal in this chapter is to bring these concepts together as we examine the quantitative aspects of acid–base chemistry. In particular we are interested in acids, bases, and their mixtures as they affect the concentration of hydronium ions in solution. As we do this, the concept of pH will be developed and used.

The principles we develop here have applications not only in traditional chemistry labs, but also in labs that investigate environmental, forensic, and biochemical problems. High-tech laboratories interested in materials science and nanotechnology often use the principles of acid–base equilibria. The consumer-oriented industries that make products such as cosmetics, foods, beverages, and cleaning chemicals all employ chemists who know that control of pH is very important in safe and effective consumer products.

17.1 | Water, pH, and "p" Notation

There are literally thousands of weak acids and bases, and their strengths vary widely. Both the acetic acid in vinegar and the carbonic acid in pressurized soda water, for example, are classified as weak. Yet carbonic acid is only about 3% as strong an acid as acetic acid. To study such differences quantitatively, we need to explore acid–base equilibria in greater depth. This requires that we first discuss a particularly important equilibrium that exists in *all* aqueous solutions—namely, the ionization of water itself.

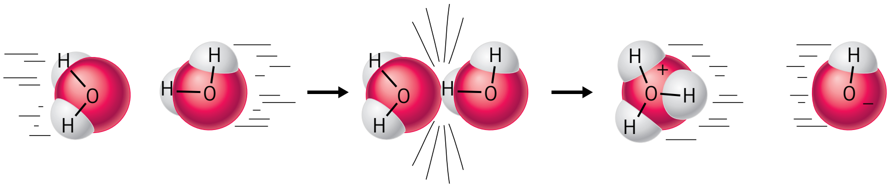
Autoionization of Water

Using sensitive instruments, pure water is observed to weakly conduct electricity, indicating the presence of very small concentrations of ions. They arise from the very slight self-ionization, or *autoionization,* of water itself, represented by the following equilibrium equation.

■ We've omitted the usual (*aq*) following the symbols for ions in water for the sake of simplicity.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

The forward reaction requires a collision of two H_2O molecules.



Its equilibrium law, following the procedures developed in Chapter 15 (i.e., we leave pure liquids, such as water in this case, out of the equilibrium law, see page 707), is

TOOLS

Ion product constant of water, K_w

$$[H_3O^+]\,[OH^-] = K_w \tag{17.1}$$

Since water is a pure liquid, with a constant 55.6 molar concentration, it does not appear in this equilibrium law. Because of the importance of the autoionization equilibrium, its equilibrium constant is given the special symbol, $\boldsymbol{K_w}$, that is called the **ion product constant of water.**

Often, for convenience, we omit the water molecule that carries the hydrogen ion and write H^+ in place of H_3O^+. The equilibrium equation for the autoionization of water then simplifies to

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equation for K_w based on this is likewise simplified.

$$\boxed{[H^+]\,[OH^-] = K_w} \tag{17.2}$$

In pure water, the concentrations of H^+ and OH^- produced by the autoionization are equal because the ions are formed in equal numbers. It's been found that the concentrations have the following values at 25 °C.

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

Therefore, at 25 °C,

$$K_w = (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7})$$
$$K_w = 1.0 \times 10^{-14} \tag{17.3}$$

As with other equilibrium constants, the value of K_w varies with temperature (see Table 17.1). Unless stated otherwise we will deal with systems at 25 °C.

Table 17.1 K_w at Various Temperatures

Temperature (°C)	K_w
0	1.5×10^{-15}
10	3.0×10^{-15}
20	6.8×10^{-15}
25	1.0×10^{-14}
30	1.5×10^{-14}
37[a]	2.5×10^{-14}
40	3.0×10^{-14}
50	5.5×10^{-14}
60	9.5×10^{-14}

[a] Normal body temperature

Effect of Solutes on $[H^+]$ and $[OH^-]$

Water's autoionization takes place in *any* aqueous solution, and because of the effects of other solutes, the molar concentrations of H^+ and OH^- may not be equal. Nevertheless, their product, K_w, is the same. Thus, although Equations 17.1–17.3 were derived for pure water, they also apply to dilute aqueous solutions. The significance of this must be emphasized. *In any aqueous solution, the product of* $[H^+]$ *and* $[OH^-]$ *equals* K_w, *although the two molar concentrations may not actually equal each other.*

Criteria for Acidic, Basic, and Neutral Solutions

One of the consequences of the autoionization of water is that *in any aqueous solution, there are always both* H_3O^+ *and* OH^- *ions, regardless of what solutes are present.* This means that in a solution of the acid HCl there is some OH^-, and in a solution of the base NaOH, there is some H_3O^+. We call a solution acidic or basic depending on which ion has the largest concentration.

A *neutral solution* is one in which the molar concentrations of H_3O^+ and OH^- are equal. An *acidic solution* is one in which some solute has made the molar concentration of H_3O^+ greater than that of OH^-. On the other hand, a *basic solution* exists when the molar concentration of OH^- exceeds that of H_3O^+.

Neutral solution $[H_3O^+] = [OH^-]$

Acidic solution $[H_3O^+] > [OH^-]$

Basic solution $[H_3O^+] < [OH^-]$

■ Because of the autoionization of water, even the most acidic solution has some OH^-, and even the most basic solution has some H_3O^+.

If we consider the autoionization constant of water, we can look at some quantitative relationships of acids and bases. For instance, we can take a solution that has an easily measurable 0.0020 *M* concentration of H_3O^+ and calculate an extremely small OH^- concentration that exists in the same solution. Rearranging Equation 17.3, we get

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ M$$

A similar calculation allows us to determine the hydronium ion concentration if we know the hydroxide ion concentration.

Practice Exercises

17.1 | Commercial, concentrated, hydrochloric acid has a concentration of 12 moles per liter. If the molarity of hydronium ions is assumed to also be 12 *M*, what is the concentration of hydroxide ions? (*Hint:* Use the relationships just discussed.)

17.2 | An aqueous solution of sodium bicarbonate, $NaHCO_3$, has a molar concentration of hydroxide ion of 7.8×10^{-6} *M*. What is the molar concentration of hydrogen ion? Is the solution acidic, basic, or neutral?

The pH Concept

In most solutions of weak acids and bases, the molar concentrations of H^+ and OH^- are very small, like those we just discussed. Writing and comparing two exponential values is not always easy. A Danish chemist, S. P. L. Sørenson (1868–1939), suggested an easier approach.

To make comparisons of small values of $[H^+]$ easier, Sørenson defined a quantity that he called the **pH** of the solution as follows.

TOOLS

Definition of pH

$$\mathrm{pH} = -\log\,[H^+] \tag{17.4}$$[1]

The properties of logarithms let us rearrange Equation 17.4 as follows.

$$[H^+] = 10^{-\mathrm{pH}} \tag{17.5}$$

Equation 17.4 can be used to calculate the pH of a solution if its molar concentration of H^+ is known. On the other hand, if the pH is known and we wish to calculate the molar concentration of hydrogen ions, we apply Equation 17.5. For example, if the hydrogen ion concentration, $[H^+]$, is 3.6×10^{-4}, we take the logarithm of this value (which is -3.44) and change its sign so that the result is a pH of 3.44. With digital calculators, it's as simple as pressing the log key and *then* changing the sign. Determining the hydrogen ion concentration using Equation 17.5 requires that we change the sign of the pH and then take the antilogarithm. For instance, if we are given a pH of 12.58 we first change it to -12.58. We then take the antilogarithm according to the instructions that came with your calculator. In this case the result is $2.6 \times 10^{-13} = [H^+]$.

■ **Calculating pH**

$$\begin{aligned}\mathrm{pH} &= -\log\,[H^+]\\ &= -\log\,(3.6 \times 10^{-4})\\ &= -(-3.44)\\ &= 3.44\end{aligned}$$

Calculating $[H^+]$

$$\begin{aligned}-\log\,[H^+] &= \mathrm{pH}\\ -\log\,[H^+] &= 12.58\\ \log\,[H^+] &= -12.58\\ [H^+] &= \mathrm{antilog}\,(-12.58)\\ [H^+] &= 10^{-12.58}\\ [H^+] &= 2.6 \times 10^{-13}\ M\end{aligned}$$

■ If you still have questions about these calculations, see the mathematics review in Appendix A.

Acidic, Basic, and Neutral Solutions

One meaning attached to pH is that it is a measure of the acidity of a solution. Hence, we may define *acidic*, *basic*, and *neutral* in terms of pH values. At 25 °C, in pure water, or in any solution that is *neutral*,

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$$

Therefore, by Equation 17.4, *the pH of a neutral solution at 25 °C is 7.00.*[2]

■ Neutral pH is 7.00 only for 25 °C. At other temperatures a neutral solution still has $[H^+] = [OH^-]$, but because K_w changes with temperature, so do the values of $[H^+]$ and $[OH^-]$. This causes the pH of the neutral solution to differ from 7.00. For example, at normal body temperature (37 °C), a neutral solution has $[H^+] = [OH^-] = 1.6 \times 10^{-7}$, so the $\mathrm{pH} = 6.80$.

An *acidic solution* is one in which $[H^+]$ is larger than 10^{-7} *M* and so has a pH *less* than 7.00. Thus, *as a solution's acidity increases, its pH decreases.*

A *basic solution* is one in which the value of $[H^+]$ is less than 10^{-7} *M* and so has a pH that is *greater* than 7.00. *As a solution's acidity decreases, its pH increases.* These simple relationships may be summarized as follows. At 25 °C:

$\mathrm{pH} = 7.00$ **Neutral solution**
$\mathrm{pH} < 7.00$ **Acidic solution**
$\mathrm{pH} > 7.00$ **Basic solution**

The pH values for some common substances are given on a pH scale in Figure 17.1.

---

[1] In this equation and similar ones, like Equation 17.6, the logarithm of only the numerical part of the bracketed term is taken. The physical units must be mol L^{-1}, but they are set aside for the calculation.

[2] Recall that the rule for significant figures in logarithms is that *the number of decimal places in the logarithm of a number equals the number of significant figures in the number.* For example, 3.2×10^{-5} has just two significant figures. The logarithm of this number, displayed on a pocket calculator, is -4.494850022. We write the logarithm, when correctly rounded, as -4.49.

One of the deceptive features of pH is how much the hydrogen ion concentration changes with a relatively small change in pH. Thus, because of the logarithmic scale, a change of one pH unit corresponds to a ten-fold change in the hydrogen ion concentration. For example, at pH 6 the hydrogen ion concentration is 1×10^{-6} mol L^{-1}. At pH 5, it's 1×10^{-5} mol L^{-1}, or ten times greater. That's a major difference.

Solutions having hydrogen ion concentrations greater than 1 *M* can be prepared and they should have negative pH values. However, at such high concentrations it is usually easier to simply write the molarity of the hydrogen ions. For example, in a solution where the value of $[H^+]$ is 2 *M*, the "2" is a simple enough number; we can't simplify it further by using its corresponding pH value. When $[H^+]$ is 2.00 *M*, the pH, calculated by Equation 17.4, would be $-\log(2.00)$ or -0.301. There is nothing wrong with negative pH values, but they offer no advantage over just writing the actual value of $[H^+]$.

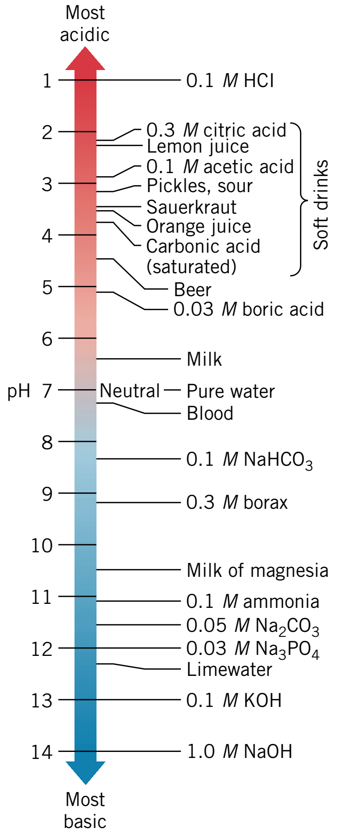


Figure 17.1 | **The pH scale.** Common substances and their approximate pH values.

"p" Notation

The logarithmic definition of pH, Equation 17.4, has proved to be so useful that it has been adapted to quantities other than $[H^+]$. Thus, for any quantity *X*, we may define a term, p*X*, in the following way.

$$pX = -\log X \tag{17.6}$$

Defining the p-function, p*X*

For example, to express small concentrations of hydroxide ion, we can define the **pOH** of a solution as

$$pOH = -\log [OH^-]$$

Similarly, for K_w we can define $\mathbf{p}\boldsymbol{K}_\mathbf{w}$ as follows.

$$pK_w = -\log K_w$$

The numerical value of pK_w at 25 °C equals $-\log(1.0 \times 10^{-14})$ or $-(-14.00)$. Thus,

$$pK_w = 14.00 \text{ (at 25 °C)}$$

A useful relationship among pH, pOH, and pK_w can be derived by taking the logarithm of all terms in Equation 17.1 or 17.2 and changing the sign to obtain Equation 17.7:

$$pH + pOH = pK_w = 14.00 \qquad \text{(at 25 °C)} \tag{17.7}$$

Relating pH and pOH to pK_w

This tells us that in an aqueous solution of any solute at 25 °C, the sum of pH and pOH is 14.00.

pH Calculations

Let's now look at some pH calculations using Equations 17.4 and 17.7. These are calculations you will be performing often in the rest of this chapter.

If we know the $[H^+]$ of a solution—let's use 6.3×10^{-5} *M* as an example—we can calculate the pH by taking the logarithm and changing the sign. The pH we calculate should be 4.20. We now have two ways to determine the pOH. Using Equation 17.2 allows us to determine $[OH^-]$, and then we can take the logarithm and change the sign to calculate the pOH. An easier method is to use Equation 17.7 and simply subtract the pH from 14.00. This subtraction tells us that the pOH must be 9.80. Equations 17.4 and 17.7 tell us that if we know one of the four terms, $[H^+]$, $[OH^-]$, pH, or pOH, we can calculate the other three. Another way to look at this helps us with solving a problem. If we are given any one of these four values, it is the same as knowing all of them. For instance, if you know the pOH but a problem requires the $[H^+]$, we know how to easily calculate the needed value. The following practice exercises make use of these calculations.

■ **Calculating pH and pOH**

$$\begin{aligned} pH &= -\log(6.3 \times 10^{-5}) \\ &= -(-4.20) \\ &= 4.20 \\ pK_w &= 14.00 = 4.20 + pOH \\ pOH &= 14.00 - 4.20 \\ &= 9.80 \end{aligned}$$

Practice Exercises

17.3 | Water draining from old coal and mineral mines often has pH values of 4.0 or lower. The cause is thought to stem from reactions of ground water and oxygen with iron pyrite, FeS. What are the pOH, $[H^+]$, and $[OH^-]$ in an acid mine drainage sample that has a pH of 4.25? (*Hint:* Recall that pH, pOH, $[H^+]$, and $[OH^-]$ are all interrelated using the K_w and pK_w.)

17.4 | Because rain washes pollutants out of the air, the lakes in many parts of the world have undergone pH changes. In a New England state, the water in one lake was found to have a hydrogen ion concentration of 3.2×10^{-5} mol L^{-1}. What are the calculated pH and pOH values of the lake's water? Is the water acidic or basic?

17.5 | Find the values of $[H^+]$ and $[OH^-]$ that correspond to each of the following values of pH. State whether each solution is acidic or basic.

(a) 2.90 (the approximate pH of lemon juice)
(b) 3.85 (the approximate pH of sauerkraut)
(c) 10.81 (the pH of milk of magnesia, an antacid)
(d) 4.11 (the pH of orange juice, on the average)
(e) 11.61 (the pH of dilute, household ammonia)

pH Meters

One of the remarkable things about pH is that it can be easily measured using an instrument called a pH meter (Figure 17.2). An electrode system sensitive to the hydrogen ion concentration in a solution is first dipped into a standard solution of known pH to calibrate the instrument. Once calibrated, the apparatus can then be used to measure the pH of any other solution simply by immersing the electrodes into it. The accuracy of pH meter measurements is usually ± 0.02 pH units.

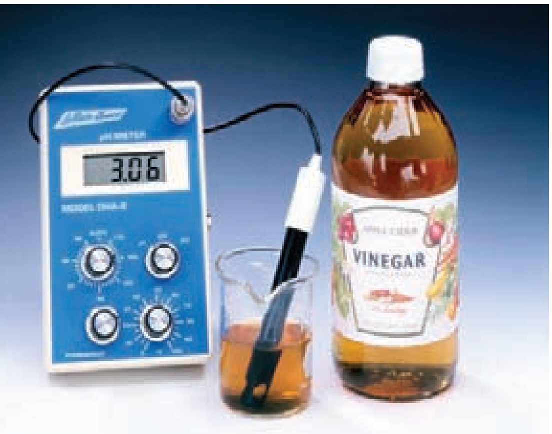


Figure 17.2 | **A pH meter.** After the instrument has been calibrated with a solution of a known pH, the combination electrode is dipped into the solution to be tested and the pH is read from the meter. *(Richard Megna/Fundamental Photographs.)*

17.2 | pH of Strong Acid and Base Solutions

Many solutes affect the pH of an aqueous solution. In this section we examine how strong acids and bases behave and how to calculate the pH of their solutions. Weak acids and bases have similar effects, which we will discuss in the next section.

Strong Acids and Bases

■ If necessary, review the list of strong acids on page 170.

In Section 16.3 we saw that strong acids and bases are considered to be 100% dissociated in an aqueous solution. This makes calculating the concentrations of H^+ and OH^- in their solutions a relatively simple task.

When the solute is a strong monoprotic acid, such as HCl or HNO_3, the molarity of H^+ will be the same as the molarity of the strong acid. Thus, a 0.010 *M* solution of HCl contains 0.010 mol L^{-1} of H^+ and a 0.0020 *M* solution of HNO_3 contains 0.0020 mol L^{-1} of H^+.

To calculate the pH of a solution of a strong monoprotic acid, we use the molarity of the H^+ obtained from the stated molar concentration of the acid. Thus, the 0.010 *M* HCl solution mentioned above has a pH of 2.00.

For strong bases, calculating the OH^- concentration is similarly straightforward. A 0.050 *M* solution of NaOH contains 0.050 mol L^{-1} of OH^- because the base is fully dissociated and each mole of NaOH releases one mole of OH^- when it dissociates. For bases such as $Ba(OH)_2$ we have to recognize that two moles of OH^- are released by each mole of the base.

$$Ba(OH)_2(s) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

Therefore, if a solution contained 0.010 mol $Ba(OH)_2$ per liter, the concentration of OH^- would be 0.020 M. Of course, once we know the OH^- concentration we can calculate pOH, from which we can calculate the pH. Working through the following practice exercises will help to solidify these methods.

Practice Exercises

17.6 | Calculate the $[H^+]$, pH, and pOH in 0.0050 M HNO_3. (*Hint:* HNO_3 is a strong acid.)

17.7 | Calculate the pOH, $[H^+]$, and pH in a solution made by weighing 1.20 g of KOH and dissolving it in sufficient water to make 250.0 mL of solution.

17.8 | Rhododendrons are shrubs that produce beautiful flowers in the springtime. They only grow well in soil that has a pH that is 5.5 or slightly lower. What is the hydrogen ion concentration in the soil moisture if the pH is 5.5?

Effect of Solute on the Ionization of Water

In the preceding calculations, we have made a critical and correct assumption—namely, that the autoionization of water contributes negligibly to the total $[H^+]$ in a solution of an acid and to the total $[OH^-]$ in a solution of a base.[3] Let's take a closer look at this.

In a solution of an acid, there are actually *two* sources of H^+. One is from the ionization of the acid itself and the other is from the autoionization of water. Thus,

$$[H^+]_{\text{total}} = [H^+]_{\text{from solute}} + [H^+]_{\text{from } H_2O}$$

■ A similar equation applies to the equilibrium OH^- concentration in a solution of a base.

$$[OH^-]_{\text{equilib}} = [OH^-]_{\text{from solute}} + [OH^-]_{\text{from } H_2O}$$

Except in very dilute solutions of acids, the amount of H^+ contributed by the water ($[H^+]_{\text{from } H_2O}$) is small compared to the amount of H^+ contributed by the acid ($[H^+]_{\text{from solute}}$). For instance, in 0.020 M HCl the molarity of OH^- is 5.0×10^{-13} M. The only source of OH^- in this acidic solution is from the autoionization of water, and the amounts of OH^- and H^+ *formed by the autoionization of water* must be equal. Therefore, $[H^+]_{\text{from } H_2O}$ also equals 5.0×10^{-13} M. If we now look at the total $[H^+]$ for this solution, we have

$$\begin{aligned}[H^+]_{\text{total}} &= \underset{\text{(from HCl)}}{0.020\ M} + \underset{\text{(from } H_2O)}{5.0 \times 10^{-13}\ M} \\ &= 0.020\ M \text{ (rounded correctly)}\end{aligned}$$

In any solution of an acid, the autoionization of water is suppressed by the H^+ furnished by the solute. It's simply an example of Le Châtelier's principle. If we look at the autoionization reaction, we can see that if some H^+ is provided by an external source (an acidic solute, for example), the position of equilibrium will be shifted to the left.

$$H_2O \rightleftharpoons H^+ + OH^-$$

Adding H^+ from a solute causes the position of equilibrium to shift to the left.

As the results of our calculation have shown, the concentrations of H^+ and OH^- *from the autoionization reaction* are reduced well below their values in a neutral solution (1.0×10^{-7} M). Therefore, except for *very* dilute solutions (10^{-6} M or less), we will assume that all of the H^+ in the solution of an acid comes from the solute. Similarly, *we'll assume that in a solution of a base, all the* OH^- *comes from the dissociation of the solute.*

---

[3] The autoionization of water cannot be neglected when working with very dilute solutions of acids and bases.

17.3 | Ionization Constants, K_a and K_b

As you've learned in Chapter 16, weak acids and bases are incompletely ionized in water and exist in solution as molecules that are in equilibria with the ions formed by their reactions with water. To deal quantitatively with these equilibria it is essential that you be able to write correct chemical equations for the equilibrium reactions, from which you can then obtain the corresponding correct equilibrium laws. Fortunately, there is a pattern that applies to the way these substances react. *Once you've learned how to write the correct equation for one acid or base, you can write the correct equation for any other.*

Reaction of a Weak Acid with Water

In aqueous solutions, all weak acids behave the same way. They are Brønsted acids and, therefore, proton donors. Some examples are $HC_2H_3O_2$, HSO_4^-, and NH_4^+. In water, these participate in the following equilibria.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Notice that in each case, the acid reacts with water to give H_3O^+ and the corresponding conjugate base. We can represent these reactions in a general way using HA to represent the formula of the weak acid and A^- to represent the anion.

TOOLS

General equation for the ionization of a weak acid

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad \textbf{(17.8)}$$

As you can see from the equations above, HA does not have to be electrically neutral; it can be a molecule such as $HC_2H_3O_2$, a negative ion such as HSO_4^- or a positive ion such as NH_4^+. (Of course, the actual charge on the conjugate base will then depend on the charge on the parent acid.)

Following the procedure developed in Chapter 15, we can also write a general equation for the equilibrium law, omitting the concentration of liquid water as usual, for Equation 17.8,

■ Some call K_a the ***acid dissociation constant.***

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a \qquad \textbf{(17.9)}$$

The new constant $\boldsymbol{K_a}$ is called an **acid ionization constant.** Abbreviating H_3O^+ as H^+, the equation for the ionization of the acid can be simplified as

$$HA \rightleftharpoons H^+ + A^-$$

from which the expression for K_a is obtained directly.

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \textbf{(17.10)}$$

You should learn how to write the chemical equation for the ionization of a weak acid and be able to write the equilibrium law corresponding to its K_a. For example, if we have a weak acid such as HNO_2 we can write the ionization reaction as

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

and the corresponding equilibrium law is

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

The meat products shown here contain nitrite ion as a preservative. *(Andy Washnik)*

Practice Exercises

17.9 | For each of the following acids, write the equation for its ionization in water and the appropriate expression for K_a: (a) $HC_2H_3O_2$, (b) $(CH_3)_3NH^+$, (c) H_3PO_4. (*Hint:* Determine the conjugate base for each of these acids.)

17.10 | For each of the following acids, write the equation for its ionization in water and the appropriate expression for K_a: (a) $HCHO_2$, (b) $(CH_3)_2NH_2^+$, (c) $H_2PO_4^-$.

For weak acids, values of K_a are usually quite small and can be conveniently represented in a logarithmic form similar to pH. Thus, we can define the **pK_a** of an acid as

$$pK_a = -\log K_a$$

The strength of a weak acid is determined by its value of K_a; the larger the K_a, the stronger and more fully ionized the acid. Because of the negative sign in the defining equation for pK_a, the stronger the acid, the *smaller* is its value of pK_a. The values of K_a and pK_a for some typical weak acids are given in Table 17.2. A more complete list is located in Appendix C.8.

- Also, K_a = antilog ($-pK_a$) or $K_a = 10^{-pK_a}$

- The values of K_a for strong acids are very large and are not tabulated. For many strong acids, K_a values have not been measured.

Practice Exercises

17.11 | Use Table 17.2 to find all the acids that are stronger than acetic acid and weaker than formic acid. (*Hint:* It may be easier to focus on the K_a values since they are directly related to acid strength.)

17.12 | Two acids, H*A* and H*B*, have pK_a values of 3.16 and 4.14, respectively. Which is the stronger acid? What are the K_a values for these acids?

Table 17.2 K_a and pK_a Values for Weak Monoprotic Acids at 25 °C

Name of Acid	Formula	K_a	pK_a
Iodic acid	HIO_3	1.7×10^{-1}	0.77
Chloroacetic acid	$HC_2H_2O_2Cl$	1.4×10^{-3}	2.85
Nitrous acid	HNO_2	4.6×10^{-4}	3.34
Hydrofluoric acid	HF	3.5×10^{-4}	3.46
Cyanic acid	$HOCN$	2×10^{-4}	3.7
Formic acid	$HCHO_2$	1.8×10^{-4}	3.74
Barbituric acid	$HC_4H_3N_2O_3$	9.8×10^{-5}	4.01
Hydrazoic acid	HN_3	2.5×10^{-5}	4.60
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	4.74
Butanoic acid	$HC_4H_7O_2$	1.5×10^{-5}	4.82
Propanoic acid	$HC_3H_5O_2$	1.3×10^{-5}	4.89
Hypochlorous acid	$HOCl$	3.0×10^{-8}	7.52
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Phenol	HC_6H_5O	1.3×10^{-10}	9.89
Hydrogen peroxide	H_2O_2	2.4×10^{-12}	11.62

Reaction of a Weak Base with Water

As with weak acids, all weak bases behave in a similar manner in water. They are weak Brønsted bases and are therefore proton acceptors. Examples are ammonia, NH_3, and acetate ion, $C_2H_3O_2^-$. Their reactions with water are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Notice that in each instance, the base reacts with water to give OH^- and the corresponding conjugate acid. We can also represent these reactions by a general equation. If we represent the base by the symbol B, the reaction is

General equation for the ionization of a weak base

$$B + H_2O \rightleftharpoons BH^+ + OH^- \tag{17.11}$$

(As with weak acids, B does not have to be electrically neutral.) This yields the equilibrium law, where water is omitted as usual. We have a new equilibrium constant that is called the **base ionization constant,** with the symbol $\boldsymbol{K_b}$.

- K_b is also called the ***base dissociation constant.***

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{17.12}$$

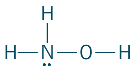
To illustrate, let's write the ionization reaction for the weak base, propylamine, $CH_3CH_2CH_2NH_2$.

$$CH_3CH_2CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2CH_2NH_3{}^+ + OH^-$$

The corresponding equilibrium law is

$$K_b = \frac{[CH_3CH_2CH_2NH_3{}^+][[OH^-]}{[CH_3CH_2CH_2NH_2]}$$

Practice Exercises



$H-\overset{\displaystyle H}{\underset{\cdot\cdot}{N}}-O-H$

hydroxylamine, NH_2OH

17.13 | For each of the following bases, write the equation for its ionization in water and the appropriate expression for K_b. (*Hint:* See Equation 17.12.) (a) $(CH_3)_3N$ (trimethylamine), (b) $SO_3{}^{2-}$ (sulfite ion), (c) NH_2OH (hydroxylamine)

17.14 | Write the ionization reaction, and the K_b expression, when each of the following amphiprotic substances acts as a base: (a) HS^-, (b) $H_2PO_4{}^-$, (c) $HPO_4{}^{2-}$, (d) $HCO_3{}^-$, (e) $HSO_3{}^-$.

Because the K_b values for weak bases are usually small numbers, the same kind of logarithmic notation is often used to represent their equilibrium constants. Thus, **p$\boldsymbol{K_b}$** is defined as

$$pK_b = -\log K_b$$

- Also, K_b = antilog $(-pK_b)$ or $K_b = 10^{-pK_b}$

Table 17.3 lists some molecular bases and their corresponding values of K_b and pK_b. A more complete list is located in Appendix C.8.

- Tables of ionization constants usually give values for only the molecular member of an acid–base pair.

Table 17.3 **K_b and pK_b Values for Weak Molecular Bases at 25 °C**

Name of Base	Formula	K_b	pK_b
Butylamine	$C_4H_9NH_2$	5.9×10^{-4}	3.23
Methylamine	CH_3NH_2	4.4×10^{-4}	3.36
Ammonia	NH_3	1.8×10^{-5}	4.74
Strychnine	$C_{21}H_{22}N_2O_2$	1.8×10^{-6}	5.74
Morphine	$C_{17}H_{19}NO_3$	1.6×10^{-6}	5.80
Hydrazine	N_2H_4	1.3×10^{-6}	5.89
Hydroxylamine	$HONH_2$	1.1×10^{-8}	7.96
Pyridine	C_5H_5N	1.7×10^{-9}	8.87
Aniline	$C_6H_5NH_2$	3.9×10^{-10}	9.41

The Product of K_a and K_b

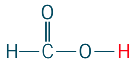
Formic acid, $HCHO_2$ (a substance partly responsible for the sting of a fire ant), is a typical weak acid that ionizes according to the equation

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

As you've seen, we write its K_a expression as

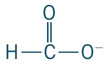
$$K_a = \frac{[H^+][CHO_2^-]}{[HCHO_2]}$$

■ Formic acid and formate ion have the structures



$$H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}H$$

formic acid, $HCHO_2$
(Acidic hydrogen shown in red.)



$$H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^-$$

formate ion, CHO_2^-

Often the formula for formic acid is written HCOOH to emphasize its molecular structure. In this chapter we will write the formulas for acids with the acidic hydrogens first in the formula, which is why we've given the formula for formic acid as $HCHO_2$.

The conjugate base of formic acid is the formate ion, CHO_2^-, and when a solute that contains this ion (e.g., $NaCHO_2$) is dissolved in water, the solution is slightly basic. In other words, the formate ion acts as a weak base since it is the conjugate base of formic acid. The reaction of formate ions with water is

$$CHO_2^- + H_2O \rightleftharpoons HCHO_2 + OH^-$$

The K_b expression for this base is

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]}$$

There is an important relationship between the equilibrium constants for this conjugate acid–base pair: the product of K_a times K_b equals K_w. We can see this by multiplying the mass action expressions above.

$$K_a \times K_b = \frac{[H^+]\cancel{[CHO_2^-]}}{\cancel{[HCHO_2]}} \times \frac{\cancel{[HCHO_2]}[OH^-]}{\cancel{[CHO_2^-]}} = [H^+][OH^-] = K_w$$

In fact, this same relationship exists for *any* acid–base conjugate pair.

For *any* acid–base conjugate pair:

$$\boxed{K_a \times K_b = K_w} \tag{17.13}$$

Inverse relationship between K_a and K_b

Another useful relationship, which can be derived by taking the negative logarithm of each side of Equation 17.13, is

$$\boxed{pK_a + pK_b = pK_w = 14.00 \qquad \text{(at 25 °C)}} \tag{17.14}$$

Relationship between pK_a and pK_b

There are some important consequences of the relationship expressed in Equation 17.13. One is that it is not necessary to tabulate both K_a and K_b for the members of an acid–base pair; if one K is known, the other can be calculated. For example, the K_a for $HCHO_2$ and the K_b for NH_3 will be found in most tables, and those tables usually will not contain the K_b for CHO_2^- or the K_a for NH_4^+. If they are needed, we can calculate them using Equation 17.13.

■ $-\log (K_a \times K_b) = -\log K_w$
$(-\log K_a) + (-\log K_b) = -\log K_w$
$pK_a + pK_b = pK_w$

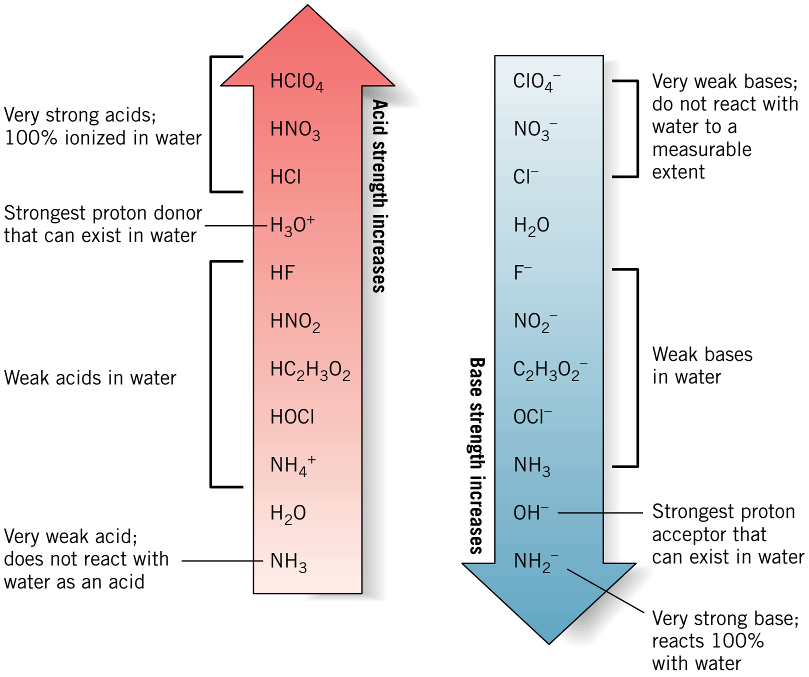
Practice Exercises

17.15 | The methylammonium ion $CH_3NH_3^+$ has a K_a of 2.3×10^{-11}. What is the K_b for the base methylamine? (*Hint:* Recall that K_a and K_b are inversely proportional to each other.)

17.16 | The value of K_b for the CHO_2^- ion is 5.5×10^{-11}. What is the value of K_a for $HCHO_2$?

Another interesting and useful observation is that *there is an inverse relationship between the strengths of the acid and base members of a conjugate pair*. This is illustrated graphically in Figure 17.3. Because the product of K_a and K_b is a constant, the larger the value of K_a the smaller is the value of K_b. In other words, *the stronger the acid, the weaker is its conjugate base* (a fact that we noted in Chapter 16 in our discussion of the strengths of Brønsted acids and bases). We will say more about this relationship in Section 17.6.

Figure 17.3 | **The relative strengths of conjugate acid–base pairs.** The stronger the acid is, the weaker is its conjugate base. The weaker the acid is, the stronger is its conjugate base. Very strong acids are 100% ionized and their conjugate bases do not react with water to any measurable extent.


Very strong acids; 100% ionized in water
Strongest proton donor that can exist in water
Weak acids in water
Very weak acid; does not react with water as an acid
$HClO_4$
HNO_3
HCl
H_3O^+
HF
HNO_2
$HC_2H_3O_2$
HOCl
NH_4^+
H_2O
NH_3
Acid strength increases
Base strength increases
ClO_4^-
NO_3^-
Cl^-
H_2O
F^-
NO_2^-
$C_2H_3O_2^-$
OCl^-
NH_3
OH^-
NH_2^-
Very weak bases; do not react with water to a measurable extent
Weak bases in water
Strongest proton acceptor that can exist in water
Very strong base; reacts 100% with water

17.4 | Determining K_a and K_b Values

Our goal in this section is to develop a general strategy for dealing quantitatively with the equilibria of weak acids and bases in water. Generally, these calculations fall into two categories. The first involves calculating the value of K_a or K_b from the initial concentration of the acid or base and the measured pH of the solution (or some other data about the equilibrium composition of the solution). The second involves calculating equilibrium concentrations given K_a or K_b and initial concentrations, which we consider in Section 17.5.

Methods Using Initial Concentrations and Equilibrium Data

In problems of this type, our *first* goal is to obtain numerical values for *all* the equilibrium concentrations that are needed to evaluate the mass action expression in the definition of K_a or K_b. (The reason, of course, is that at equilibrium the reaction quotient, Q, equals the equilibrium constant.) We are usually given the molar concentration of the acid or base as it would appear on the label of a bottle containing the solution. Also provided is information from which we can obtain directly at least one of the equilibrium concentrations. Thus, we might be given the measured pH of the solution, which provides an estimate of the equilibrium concentration of H^+. (Equilibrium is achieved rapidly in these solutions, so when we measure the pH, the value obtained can be used to calculate the equilibrium concentration of H^+.) Alternatively, we might be given the **percentage ionization** of the acid or base, which we define as follows:

TOOLS

Percentage ionization

$$\text{percentage ionization} = \frac{\text{moles ionized per liter}}{\text{moles available per liter}} \times 100\% \qquad \textbf{(17.15)}$$

Let's look at some examples that illustrate how to determine K_a and K_b from the kind of data mentioned.

Example 17.1

Calculating K_a and pK_a from pH

Lactic acid ($HC_3H_5O_3$), which is present in sour milk, also gives sauerkraut its tartness. It is a monoprotic acid. In a 0.100 *M* solution of lactic acid, the pH is 2.44 at 25 °C. Calculate the K_a and pK_a for lactic acid at this temperature.

For some, nothing goes better on a hot dog than sauerkraut and mustard. Lactic acid gives sauerkraut its sour taste. *(Susan Kaprov)*

Analysis: In any problem involving the ionization of a weak acid or base, the first step is to write the balanced chemical equation. From the equation we can write the correct equilibrium law and perform any necessary stoichiometric reasoning, with the help of a concentration table if needed.

We're given the pH of the solution, so we can use this to calculate the H^+ concentration. This will be the *equilibrium* [H^+]; as noted previously, equilibrium is reached rapidly in solutions of acids and bases. (It's important to remember that values that satisfy the K_a expression are *equilibrium* values only.)

Assembling the Tools: We're told it's an acid, so we'll begin by writing the equilibrium equation, and then the K_a expression, as we have done in the practice exercises,

$$HC_3H_5O_3 \rightleftharpoons H^+ + C_3H_5O_3^- \qquad K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

Equation 17.5 is needed to calculate [H^+], and we will construct and use a concentration table using Example 15.8 on page 720 as our guide.

Solution: Looking at our tools, we see that we need the equilibrium values for [H^+], [$C_3H_5O_3^-$], and [$HC_3H_5O_3$] to calculate K_a. At this point it will help to set up a concentration table. To obtain the initial concentrations we see that the only solute is $HC_3H_5O_3$, (0.100 *M*), so the only source of the ions, H^+ and $C_3H_5O_3^-$, is the ionization of the acid. Their concentrations are listed initially as zero. (Remember that, in a solution of an acid, it is safe to ignore the small amount of H^+ contributed by the autoionization of water.) As we did in Example 15.8, the change in concentrations will be represented as the unknown *x*. Adding the initial concentration and change rows gives us the terms for the equilibrium concentrations. These entries are shown in black.

We now find the [H^+] from pH. This gives us the *equilibrium* value of [H^+].

Remember, the measured pH *always* gives the equilibrium concentration of H^+.

$$[H^+] = 10^{-2.44}$$
$$= 0.0036\ M$$

This value is the equilibrium concentration of H^+ (shown in red). From this we see that *x* must be 0.0036. Knowing *x*, we can calculate the equilibrium concentrations of $HC_3H_5O_3$ and $C_3H_5O_3^-$ as shown in green in the table.

	$HC_3H_5O_3$	$\rightleftharpoons$	H^+	+	$C_3H_5O_3^-$
Initial concentrations (*M*)	0.100		0		0
Changes in concentrations (*M*)	$-x$		$+x$		$+x$
Equilibrium conc. (*M*)	$(0.100 - x)$		x		x
Equilibrium concentration values based on pH	$(0.100 - 0.0036) = 0.096$ (correctly rounded)		0.0036		0.0036

The last row of data now contains the equilibrium concentrations that we now use to calculate K_a. We simply substitute them into the K_a expression.

$$K_a = \frac{(3.6 \times 10^{-3})(3.6 \times 10^{-3})}{0.096} = 1.4 \times 10^{-4}$$

Thus the acid ionization constant for lactic acid is 1.4×10^{-4}. To find pK_a, we take the negative logarithm of K_a.

$$pK_a = -\log K_a = -\log (1.4 \times 10^{-4}) = 3.85$$

Is the Answer Reasonable? Weak acids have small ionization constants, so the value we obtained for K_a seems to be reasonable. *We should also check the entries in the concentration table to be sure they are reasonable.* For example, the "changes" for the ions are both positive, meaning both of their concentrations are increasing. This is the way it *must* be because neither ion can have a concentration less than zero. The changes are caused by the ionization reaction, so they both have to change in the same direction. Also, we have the concentration of the molecular acid decreasing, as it should if the ions are being formed by the ionization.

Sometimes we have the opportunity to determine the percentage ionization of a substance. Obvious examples are osmotic pressure measurements and measurements of freezing point depression and boiling point elevations that we discussed in Section 13.7. The following example illustrates how we can determine the value of K_b of a base such as methylamine when we know its percentage ionization.

Example 17.2

Calculating K_b and pK_b from the Percentage Ionization

Methylamine is responsible in part for the fishy aroma of pickled herring. *(Andy Washnik)*

Methylamine, CH_3NH_2, is a weak base and one of several substances that give herring brine its pungent odor. In 0.100 *M* CH_3NH_2, only 6.4% of the base is ionized. What are K_b and pK_b of methylamine?

Analysis: In this problem we've been given the percentage ionization of the base. We will use this to calculate the equilibrium concentrations of the ions in the solution. After we know these, solving the problem follows the same path as in the preceding example.

Assembling the Tools: As in the previous example, we need the balanced chemical equation (see the format for a weak base in Equation 17.11) so we can write the equilibrium law (see the format for the equilibrium law of a weak base in Equation 17.12). These are written as

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

We will also use the percentage ionization, Equation 17.15, to calculate at least one of the equilibrium concentrations.

Solution: Now that we have our tools, we can start constructing the equilibrium table with the chemical equation and the appropriate rows and columns. We next enter the initial concentrations as shown in black. The initial concentrations are those concentrations before any reaction takes place. Therefore the concentrations of the ions are listed as zeros. Usually, we use the variable *x* to indicate the changes expected, in the change row, and the equilibrium concentrations in the last row, which we recall is the sum of the first two rows. However, the percentage composition allows us to complete the table directly.

The percentage ionization tells us that 6.4% of the CH_3NH_2 has reacted. Entering the information into Equation 17.15 gives us

$$\frac{\text{moles per liter of } CH_3NH_2 \text{ ionized}}{0.100\ M} \times 100\% = 6.4\%$$

Therefore, the number of moles per liter of the base that has ionized at equilibrium in this solution is:

$$\text{moles per liter of } CH_3NH_2 \text{ ionized} = \frac{6.4\% \times 0.100\ M}{100\%} = 0.0064\ M$$

■ To find 6.4% of 0.100 *M*, Equation 17.15 has been rearranged.

This value represents the *decrease* in the concentration of CH_3NH_2, which is -0.0064 moles L^{-1} of CH_3NH_2. We can now use this change in $[CH_3NH_2]$ to determine the concentrations of the other species. We find that $[CH_3NH_2{}^+]$ and $[OH^-]$ are both 0.0064 mol L^{-1}. Let's enter these values directly into the concentration table.

	H_2O	+	CH_3NH_2	$\rightleftharpoons$	$CH_3NH_3{}^+$	+	OH^-
Initial concentrations (*M*)			0.100		0		0
Changes in concentrations (*M*)			−0.0064		0.0064		0.0064
Equilibrium conc. (*M*)			(0.100 − 0.0064)		0.0064		0.0064

Now we can calculate K_b by substituting equilibrium quantities into the mass action expression.

$$K_b = \frac{(0.0064)(0.0064)}{(0.100 - 0.0064)} = 4.4 \times 10^{-4}$$

and

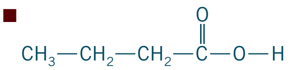
$$pK_b = -\log(4.4 \times 10^{-4}) = 3.36$$

■ **Is the Answer Reasonable?** First, the value of K_b is small, so that suggests we've probably worked the problem correctly. We can also check the "Change" row to be sure the algebraic signs are correct. Both initial concentrations start out at zero, so they must both increase, which they do. The change for the CH_3NH_2 is opposite in sign to that for the ions, and that's as it should be. Therefore, we appear to have set up the problem correctly.

Practice Exercises

17.17 | Salicylic acid reacts with acetic acid to form aspirin, acetyl salicylic acid. A 0.200 molar solution of salicylic acid has a pH of 1.83. Calculate the K_a and pK_a of salicylic acid. (*Hint:* Convert the pH to $[H^+]$ first.)

17.18 | When butter turns rancid, its foul odor is mostly that of butanoic acid, $HC_4C_7O_2$, a weak monoprotic acid similar to acetic acid in structure. In a 0.0100 *M* solution of butanoic acid at 20 °C, the acid is 4.0% ionized. Calculate the K_a and pK_a of butanoic acid at this temperature.

■ 
$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H$

butanoic acid
$HC_4H_7O_2$

17.19 | Few substances are more effective in relieving intense pain than morphine. Morphine is an alkaloid—an alkali-like compound obtained from plants—and alkaloids are all weak bases. In 0.010 *M* morphine, the pOH is 3.90. Calculate the K_b and pK_b for morphine. (You don't need to know the formula for morphine, just that it's a base. Use whatever symbol you want to write the equation.)

17.5 | pH of Weak Acid and Weak Base Solutions

It is interesting to understand some methods for determining the K_a and K_b values. Someday you may synthesize an acid or base and have the need to characterize its properties by such an analysis. However, it is more common to use those values for everyday laboratory calculations of pH or $[H^+]$.

Calculating Equilibrium Concentrations

These calculations are not especially difficult, providing you start off on the right foot. The key to success is examining the statement of the problem carefully so you can construct the correct chemical equation, which will then lead you to write the equilibrium law that's required to obtain the solution. With this in mind, let's take an overview of the "landscape" to develop a method for selecting the correct approach to the problem.

Almost any problem in which you are given a value of K_a or K_b falls into one of three categories: (1) the aqueous solution contains a weak acid as its *only* solute, (2) the solution contains a weak base as its *only* solute, or (3) the solution contains *both* a weak acid and its conjugate base. The approach we take for each of these conditions is described below and is summarized in Figure 17.4.

1. If the solution contains only a weak acid as the solute, then the problem *must* be solved using K_a. This means that the correct chemical equation for the problem is the ionization of the weak acid. It also means that if you are given the K_b for the acid's conjugate base, you will have to calculate the K_a using Equation 17.13 in order to solve the problem.
2. If the solution contains only a weak base, the problem *must* be solved using K_b. The correct chemical equation is for the ionization of the weak base. If the problem gives you K_a for the base's conjugate acid, then you must use Equation 17.13 to calculate K_b to solve the problem.

■ Conditions 1 and 2 apply to solutions of weak molecular acids and bases and to solutions of salts that contain an ion that is an acid or a base. Condition 3 applies to solutions called *buffers*, which are discussed in Section 17.7.

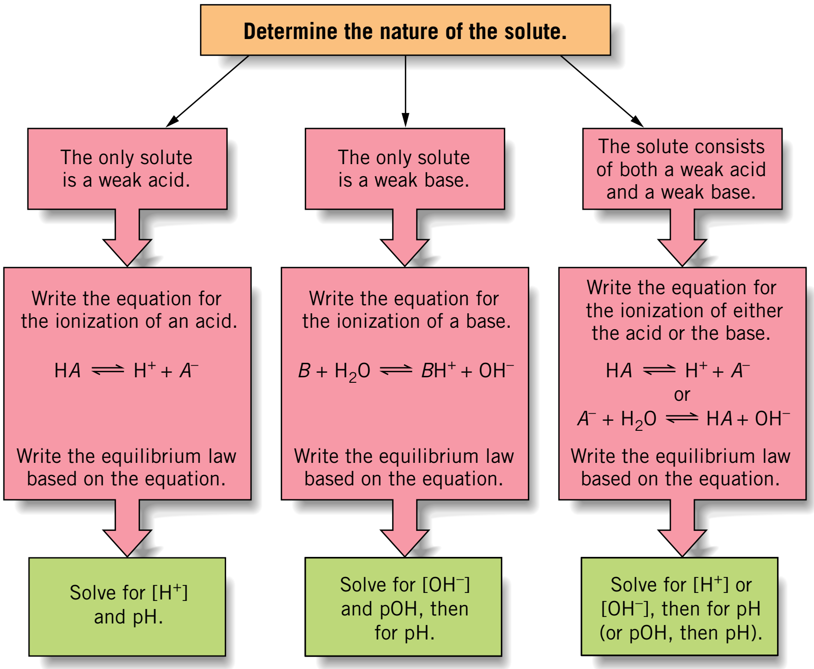

Determine the nature of the solute.
The only solute is a weak acid.
The only solute is a weak base.
The solute consists of both a weak acid and a weak base.
Write the equation for the ionization of an acid.
$HA \rightleftharpoons H^+ + A^-$
Write the equilibrium law based on the equation.
Write the equation for the ionization of a base.
$B + H_2O \rightleftharpoons BH^+ + OH^-$
Write the equilibrium law based on the equation.
Write the equation for the ionization of either the acid or the base.
$HA \rightleftharpoons H^+ + A^-$
or
$A^- + H_2O \rightleftharpoons HA + OH^-$
Write the equilibrium law based on the equation.
Solve for $[H^+]$ and pH.
Solve for $[OH^-]$ and pOH, then for pH.
Solve for $[H^+]$ or $[OH^-]$, then for pH (or pOH, then pH).

Figure 17.4 | **Determining how to proceed in acid–base equilibrium problems.** The nature of the solute species determines how the problem is approached. Following this diagram will get you started in the right direction.

3. Solutions that contain two solutes, one a weak acid and the other its conjugate base, have some special properties that we will discuss later. (Such solutions are called *buffers.*) To work problems for these kinds of mixtures, we can use *either* K_a or K_b—it doesn't matter which we use, because we will obtain the same answers either way. However, if we elect to use K_a, then the chemical equation we use must be for the ionization of the acid. If we decide to use K_b, then the correct chemical equation is for the ionization of the base. Usually, the choice of whether to use K_a or K_b is made on the basis of which constant is most readily available.

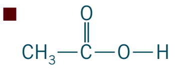
When you begin to solve a problem, decide which of the three conditions above applies. If necessary, keep Figure 17.4 handy to guide you in your decision, so that you select the correct path to follow.

Simplifications in Calculations

In Chapter 15 you learned that when the equilibrium constant is small, it is frequently possible to make simplifying assumptions that greatly reduce the algebraic effort in obtaining equilibrium concentrations. For many acid–base equilibrium problems such simplifications are particularly useful.

Let's consider a solution of 1.0 *M* acetic acid, $HC_2H_3O_2$, for which $K_a = 1.8 \times 10^{-5}$. What is involved in determining the equilibrium concentrations in the solution?

To answer this question, we begin with the chemical equation for the equilibrium. Because the only solute in the solution is the weak acid, we must use K_a and therefore write the equation for the ionization of the acid. Let's use the simplified version.



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

acetic acid
$HC_2H_3O_2$

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

The equilibrium law is

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

We will take the given concentration, 1.0 *M*, to be the initial concentration of $HC_2H_3O_2$ (i.e., the concentration of the acid before any ionization has occurred). This concentration will decrease slightly as the acid ionizes and the ions form. If we let x be the amount of acetic acid that ionizes per liter, then the $HC_2H_3O_2$ concentration will decrease by x (its change will be $-x$) and the H^+ and $C_2H_3O_2^-$ concentrations will each increase by x (their changes will be $+x$). We can now construct the following concentration table.

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	$+$	$C_2H_3O_2^-$
Initial concentrations (*M*)	1.0		0		0
Changes in concentrations (*M*)	$-x$		$+x$		$+x$
Equilibrium conc. (*M*)	$1.0 - x$		x		x

The initial concentrations of the ions are set equal to zero because none of them have been supplied by a solute.

The values in the last row of the table should satisfy the equilibrium law. When they are substituted into the mass action expression we obtain

$$\frac{(x)(x)}{1.0 - x} = 1.8 \times 10^{-5}$$

This equation involves a term in x^2, and it could be solved using the quadratic formula as we did in Chapter 15. However, this and many other similar calculations involving weak acids and bases can be simplified. Let's look at the reasoning.

The equilibrium constant, 1.8×10^{-5}, is quite small, so we can anticipate that very little of the acetic acid will be ionized at equilibrium. This means x will be very small, so we make the approximation $(1.0 - x) \approx 1.0$. Replacing $1.0 - x$ with 1.0 yields the equation (See Section 15.8, page 726, where we first introduced this type of approximation.)

■ We are assuming that when x is subtracted from 1.0 and *the result is rounded to the correct number of significant figures*, the answer will round to 1.0.

$$\frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0} = 1.8 \times 10^{-5}$$

Solving for x gives $x = 0.0042\ M$. We see that the value of x is indeed negligible compared to 1.0 M (i.e., if we subtract 0.0042 M from 1.0 M and round correctly, we obtain 1.0 M).

Notice that when we make this approximation, *the initial concentration of the acid is used as if it were the equilibrium concentration.* The approximation is valid when the equilibrium constant is small and the concentrations of the solutes are reasonably high—conditions that will apply to most situations you will encounter in this chapter. After a few examples we will discuss the conditions under which these approximations are not valid.

Let's look at some typical acid–base equilibrium problems.

Example 17.3

Calculating the Values of $[H^+]$ and pH of a Weak Acid Solution from Its K_a Value and Initial Concentration

The calcium salt of propionic acid, calcium propionate, is used as a preservative in baked products. *(Andy Washnik)*

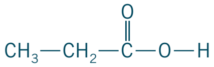
A student planned an experiment that would use 0.10 M propionic acid, $HC_3H_5O_2$. Calculate the value of $[H^+]$ and the pH for this solution. For propionic acid, $K_a = 1.3 \times 10^{-5}$.

■ **Analysis:** First, we note that the only solute in the solution is a weak acid, so we know we will have to use K_a and write the equation for the ionization of the acid.

■ **Assembling the Tools:** The balanced equation and equilibrium law we need are

$$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^-$$

$$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]}$$

■ 

$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H$$

propionic acid

$HC_3H_5O_2$

We will calculate the $[H^+]$, starting with the concentration table, and then use Equation 17.4 to obtain the pH.

■ **Solution:** We'll start off by making a concentration table using the methods described above. In this table the initial concentration of the acid is 0.10 M, and the initial concentrations of the ions are both 0 M. These values are entered in the first line of the table.

	$HC_3H_5O_2$	$\rightleftharpoons$	H^+	+	$C_3H_5O_2^-$
Initial concentrations (M)	0.10		0		0
Changes in concentrations (M)	$-x$		$+x$		$+x$
Equilibrium conc. (M)	$(0.10 - x) \approx 0.10$		x		x

From the balanced chemical equation we know that the equilibrium concentrations of H^+ and $C_3H_5O_2^-$ are the same; they are represented by x. Anticipating that x will be very small, we make the simplifying approximation $(0.10 - x) \approx 0.10$, so we take the equilibrium concentration of $HC_3H_5O_2$ to be 0.10 *M*. Substituting these quantities into the K_a expression gives

$$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{(x)(x)}{(0.10)} = 1.3 \times 10^{-5}$$

Solving for x yields

$$x = 1.2 \times 10^{-3}$$

Because $x = [H^+]$,

$$[H^+] = 1.2 \times 10^{-3}\ M$$

Finally, we calculate the pH

$$\begin{aligned} pH &= -\log(1.2 \times 10^{-3}) \\ &= 2.92 \end{aligned}$$

■ **Is the Answer Reasonable?** First, we check to be sure our assumption was reasonable, and it is (0.10 − 0.0012 = 0.10 when rounded correctly). Also we see that the calculated pH is less than 7. This tells us that the solution is acidic, which it should be for a solution of an acid. Also, the pH is higher than it would be if the acid were strong. (A 0.10 *M* solution of a strong acid would have $[H^+] = 0.10\ M$ and pH = 1.0.) If we wish to further check the accuracy of the calculation, we can substitute the calculated equilibrium concentrations into the mass action expression. If the calculated quantities are correct, the reaction quotient should equal K_a. Let's do the calculation.

$$\frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{(x)(x)}{(0.10)} = \frac{(1.2 \times 10^{-3})^2}{0.10} = 1.4 \times 10^{-5} = K_a$$

This is very close to the given K_a and we judge that we have done the calculation correctly.

Practice Exercises

17.20 | Benzoic acid, $HC_6H_5CO_2$, is a monoprotic acid (only one H^+ ionizes) with a $K_a = 6.5 \times 10^{-5}$. Calculate $[H^+]$ and the pH of a 0.023 *M* solution of benzoic acid. (*Hint:* Consider using an assumption to solve this rather than the quadratic formula.)

17.21 | Nicotinic acid, $HC_6H_4NO_2$, is a B vitamin. It is also a weak acid with $K_a = 1.4 \times 10^{-5}$. Calculate $[H^+]$ and the pH of a 0.050 *M* solution of $HC_2H_4NO_2$.

When we have the initial concentration of a molecular base, the determination of pH involves the same steps as we used in Example 17.3. However, we need to be careful to remember that the calculation yields the hydroxide ion concentration. That requires an additional conversion step from pOH to pH as shown in the following example.

Example 17.4

Calculating the pH of a Solution and the Percentage Ionization of the Solute

A solution of hydrazine, N_2H_4, has a concentration of 0.25 *M*. What is the pH of the solution, and what is the percentage ionization of the hydrazine? Hydrazine has $K_b = 1.3 \times 10^{-6}$.

■ **Analysis:** Hydrazine must be a weak base, because we have its value of K_b (the "b" in K_b tells us this is a *base* ionization constant). Since hydrazine is the only solute in the solution, we will have to write the equation for the ionization of a weak base and then set up the K_b expression.

Assembling the Tools: To write the chemical equation we need the formula for the conjugate acid of N_2H_4. It has one additional H^+, so its formula is $N_2H_5^+$. Now we write the balanced chemical equation and the equilibrium law as

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]}$$

We will use a concentration table and appropriate assumptions.

To calculate the percentage ionization, we need to use Equation 17.15 on page 784. This requires that we determine the number of moles per liter of the base that has ionized. The concentration table will help us perform this calculation correctly.

Solution: Let's once again construct the concentration table. The only sources of $N_2H_5^+$ and OH^- are the ionization of the N_2H_4, so their initial concentrations are both zero. They will form in equal amounts, so we let their changes in concentration equal $+x$. The concentration of N_2H_4 will decrease by x, so its change is $-x$.

	H_2O +	N_2H_4	$\rightleftharpoons$	$N_2H_5^+$	+	OH^-
Initial concentrations (M)		0.25		0		0
Changes in concentrations (M)		$-x$		$+x$		$+x$
Equilibrium conc. (M)		$(0.25 - x) \approx 0.25$		x		x

Because K_b is so small, $[N_2H_4] \approx 0.25\ M$. (As before, we assume the initial concentration will be effectively the same as the equilibrium concentration, an approximation that we expect to be valid.) Substituting into the K_b expression,

$$\frac{(x)(x)}{0.25 - x} \approx \frac{(x)(x)}{0.25} = 1.3 \times 10^{-6}$$

Solving for x gives: $x = 5.7 \times 10^{-4}$. This value represents the hydroxide ion concentration, from which we can calculate the pOH.

$$\text{pOH} = -\log(5.7 \times 10^{-4}) = 3.24$$

The pH of the solution can then be obtained from the relationship

$$\text{pH} + \text{pOH} = 14.00$$

Thus,

$$\text{pH} = 14.00 - 3.24 = 10.76$$

For the percent ionization we look to the concentration table and see that the value of x represents the amount of N_2H_4 that ionizes per liter (i.e., the change in the N_2H_4 concentration). Therefore,

$$\text{percentage ionization} = \frac{5.7 \times 10^{-4}\ M}{0.25\ M} \times 100\% = 0.23\%$$

The base is 0.23% ionized.

Are the Answers Reasonable? First, we can quickly check to see whether the value of x satisfies our assumption and it does $(0.25 - 0.00057 = 0.25)$. The value of the hydroxide ion concentration is small and the pH indicates a basic solution. Additionally the small concentration of hydroxide ions agrees with the small percentage ionization we calculated. We could use our equilibrium concentrations to calculate K_b as in the previous example.

Practice Exercises

17.22 | Aniline, $C_6H_5NH_2$, is a precursor for many dyes used to color fabrics, known as aniline dyes. Aniline has a K_b of 3.9×10^{-10}. What is the pOH of a 0.025 molar solution of aniline? (*Hint:* Calculate the OH^- concentration.)

17.23 | Pyridine, C_5H_5N, is a bad-smelling liquid for which $K_b = 1.7 \times 10^{-9}$. What is the pH of a 0.010 M aqueous solution of pyridine?

17.24 | Phenol is an acidic organic compound for which $K_a = 1.3 \times 10^{-10}$. What is the pH of a 0.15 M solution of phenol in water?

When Simplifications Fail

In the examples we studied above, we made a simplification by assuming that we could use the initial concentration as the equilibrium concentration of the weak acid or weak base. We confirmed this assumption by observing that, if we correctly used the significant figure rules for subtraction, the initial concentration did not change when we accounted for the amount that ionized.

In some instances, we will calculate an answer where the initial concentration will change slightly when we subtract the amount that ionizes. In those cases we may want to use the quadratic formula or the method of successive approximations described in Appendix A.4. Since these two methods are tedious and have more steps that can introduce error, we might consider relaxing the rules for using our simplifications.

■ If the simplifications do not work, we can solve quadratic equations by using the quadratic formula. A detailed description of how to use the quadratic formula is given in Chapter 15, Example 15.10 on page 724.

When we ask ourselves how precise our pH calculations need to be, we find two factors to consider. First, most ionization constants only have two significant figures, therefore the hydrogen ion concentrations we calculate should have two significant figures. We recall that the uncertainty is usually taken as ±1 in the last digit of a measurement. The uncertainty of a two-digit number ranges from 1% to 10%. Second, the experimental determination of pH usually has an uncertainty of ± 0.02 pH units or ±5% in terms of hydrogen ion concentration. In general, there is usually little need to calculate a pH more precisely than we can measure it in the laboratory. These two sources of error tell us that any simplification that results in an error less than approximately ±5% will give us acceptable results. Without going into the detailed explanation, we find a simple rule for testing if a simplification will work. The rule states that a simplifying assumption will work if the initial concentration of a weak acid, C_{HA}, or a weak base, C_B, is more than 100 times the value of the ionization constant.[4]

$$C_{HA} > 100 \times K_a \qquad \text{or} \qquad C_B > 100 \times K_b$$

TOOLS

Criteria for predicting when simplifying assumptions will work

Since we can easily multiply a K_a or K_b by 100, we can test to see if our assumptions will work *before* we do the calculation.

17.6 | pH of Salt Solutions

When we study solutions of salts, we find that many have a neutral pH. Examples are NaCl and KNO_3. However, not all salt solutions behave this way. Some, such as $NaC_2H_3O_2$, are slightly basic while others, such as NH_4Cl, are slightly acidic. To understand this behavior, we have to examine how the ions of a salt can affect the pH of a solution.

In Section 17.3 you saw that weak acids and bases are not limited to molecular substances. For instance, $NH_4{}^+$ was given as an example of a weak acid, and $C_2H_3O_2{}^-$ was

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[4] If we calculate the hydrogen ion concentration analytically, using the quadratic formula, we obtain the "true" value. We can compare that value to the concentration obtained by using a simplification and calculate the error as

$$\frac{[H^+]_{\text{simplification}} - [H^+]_{\text{quadratic}}}{[H^+]_{\text{quadratic}}} \times 100\% = \%\ \text{error}$$

When we relate this percent error to the ratio of C_a/K_a it is found that when this ratio is greater than 100, the error is less than approximately 5%.

cited as an example of a weak base. Ions such as these always come to us in compounds in which there are both a cation *and* an anion. Therefore, to place NH_4^+ in water, we need a salt such as NH_4Cl, and to place $C_2H_3O_2^-$ in water, we need a salt such as $NaC_2H_3O_2$.

Because a salt contains two ions, the pH of its solution can potentially be affected by either the cation or the anion, or perhaps even both. Therefore, we have to consider *both* ions if we wish to predict the effect of a salt on the pH of a solution.

Acidic Cations

If the cation of a salt is able to influence the pH of a solution, it does so by behaving as a weak acid. Not all cations are acidic, however, so let's look at the possibilities.

■ The reaction of a salt with water to give either an acidic or basic solution is sometimes called **hydrolysis**. Hydrolysis means *reaction with water.*

Conjugate Acids of Molecular Bases

The ammonium ion, NH_4^+, is the conjugate acid of the molecular base, NH_3. We have already learned that NH_4^+, supplied for example by NH_4Cl, is a weak acid. As seen in Figure 17.5, solutions of this salt have a pH lower than 7. The equation for the reaction as an acid is

$$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Writing this in a simplified form, along with the K_a expression, we have

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

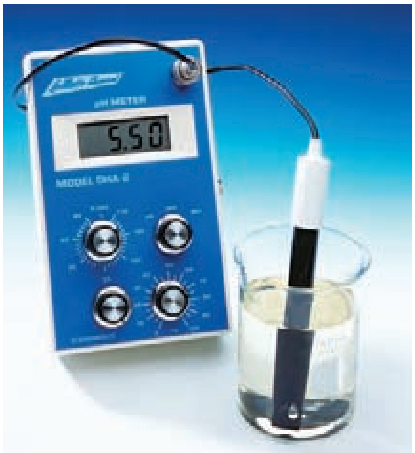


Figure 17.5 | **Ammonium ion as a weak acid.** The measured pH of a solution of the salt NH_4NO_3 is less than 7, which indicates the solution is acidic. Bromothymol blue, a pH indicator discussed in Section 17.9 (page 816) has been added and has a faint yellow color indicating an acid solution. *(Richard Megna/Fundamental Photographs.)*

Because the K_a values for ions are seldom tabulated, we would usually expect to calculate the K_a value using the relationship: $K_a \times K_b = K_w$. In Table 17.3 the K_b for NH_3 is given as 1.8×10^{-5}. Therefore,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Another example is the hydrazinium ion, $N_2H_5^+$, which is also a weak acid.

$$N_2H_5^+(aq) \rightleftharpoons N_2H_4(aq) + H^+(aq) \qquad K_a = \frac{[N_2H_4][H^+]}{[N_2H_5^+]}$$

The tabulated K_b for N_2H_4 is 1.3×10^{-6}. From this, the calculated value of K_a equals 7.7×10^{-9}.

These examples illustrate a general phenomenon:

TOOLS

Identifying acidic cations

| Cations that are the conjugate acids of molecular bases tend to be weakly acidic.

Cations that are not conjugate acids of molecular bases are generally metal ions such as Na^+, K^+, and Ca^{2+}. In Chapter 16 we learned that the cations of the Group 1A metals are extremely weak acids and are unable to affect the pH of a solution. Except for Be^{2+}, the cations of Group 2A also do not affect pH.

Basic Anions

When a Brønsted acid loses a proton, its conjugate base is formed. Thus Cl^- is the conjugate base of HCl, and $C_2H_3O_2^-$ is the conjugate base of $HC_2H_3O_2$.

$$HCl + H_2O \longrightarrow Cl^- + H_3O^+$$
$$HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+$$

Although both Cl^- and $C_2H_3O_2^-$ are bases, only the latter affects the pH of an aqueous solution. Our knowledge of conjugate acid–base pairs from Chapter 16 helps us undertand why.

Earlier you learned that there is an inverse relationship between the strength of an acid and its conjugate base—the stronger the acid, the weaker is the conjugate base. Therefore, when an acid is *extremely strong*, as in the case of HCl or other "strong" acids that are 100% ionized (such as HNO_3), the conjugate base is *extremely weak*—too weak to affect in a measurable way the pH of a solution. Consequently, we have the following generalization:

> The anion of a strong acid is too weak a base to influence the pH of a solution.

Acetic acid is much weaker than HCl, as evidenced by its value of K_a (1.8×10^{-5}). Because acetic acid is a weak acid, its conjugate base is much stronger than Cl^- and we can expect it to affect the pH (Figure 17.6). We can calculate the value of K_b for $C_2H_3O_2^-$ from the K_a for $HC_2H_3O_2$, also with the equation $K_a \times K_b = K_w$.

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

This leads to another conclusion:

> The anion of a weak acid is a weak base and can influence the pH of a solution. It will tend to make the solution basic.

TOOLS

Identifying basic anions

Acid–Base Properties of Salts

To decide if any given salt will affect the pH of an aqueous solution, we must examine each of its ions and see what it alone might do. There are four possibilities:

1. If neither the cation nor the anion can affect the pH, the solution should be neutral.
2. If only the cation of the salt is acidic, the solution will be acidic.
3. If only the anion of the salt is basic, the solution will be basic.
4. If a salt has a cation that is acidic and an anion that is basic, the pH of the solution is determined by the *relative* strengths of the acid and base based on the K_a and K_b of the ions.

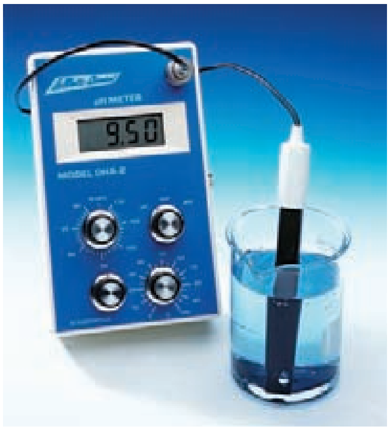


Figure 17.6 | **Acetate ion is a weak base in water.** The pH of a solution of $KC_2H_3O_2$ is greater than 7. Bromothymol blue has been added and has a blue color indicating a basic solution. *(Richard Megna/Fundamental Photographs.)*

Let's consider two salts, sodium hypochlorite, NaOCl, and calcium nitrate, $Ca(NO_3)_2$, and see how we predict if their solutions will be acidic, basic, or neutral. We can write the equations for dissolving both salts as

$$\mathrm{NaOCl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na}^+(aq) + \mathrm{OCl}^-(aq)$$
$$\mathrm{Ca(NO_3)_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ca}^{2+}(aq) + 2\mathrm{NO_3}^-(aq)$$

Now we consider whether or not each ion is related to a weak acid (for anions) or to a weak base (for cations). For the two anions, if we add a hydrogen ion to each, we can identify the acid that they are related to, HOCl and HNO_3. HNO_3 is one of our strong acids so the NO_3^- ion will not affect the pH of a solution. The HOCl on the other hand is a weak acid and will produce the conjugate base OCl^-. Turning our attention to the cations, we can see that the two cations are in Groups 1A and 2A, respectively, and are extremely weak acids that do not affect the pH of a solution. Finally, of all four ions, only the OCl^- will affect the pH. We identified the hypochlorite ion as a conjugate base and therefore its solution will be basic. Calcium nitrate solutions will be neutral since neither ion affects the pH. Neutral salts will have a pH of 7.00.

■ The only time an anion might be acidic is if it is from a partially neutralized polyprotic acid—for example HSO_4^-.

Practice Exercises

17.25 | Are solutions of (a) $NaNO_2$, (b) KCl, and (c) NH_4Br acidic, basic, or neutral? (*Hint:* Write the ions for these compounds. What are the conjugate acids and bases of these ions?)

17.26 | Are solutions of (a) $NaNO_3$, (b) KOCl, and (c) NH_4NO_3 acidic, basic, or neutral?

Now that we have reinforced the concept that anions are conjugate bases and cations are conjugate acids, we can calculate the pH of their solutions. This will be done in exactly the same way in which we calculated the pH of solutions containing weak molecular acids or weak molecular bases.

Example 17.5
Calculating the pH of a Salt Solution

Household bleach used for washing clothes, and also mildew and moss from buildings and outdoor furniture, is a solution of sodium hypochlorite, NaOCl. What is the pH of a 0.10 *M* solution of NaOCl? For HOCl, $K_a = 3.0 \times 10^{-8}$.

■ **Analysis:** Problems such as this are just like the other acid–base equilibrium problems you have learned to solve. We proceed as follows: (1) We determine the nature of the solute: is it a weak acid, a weak base, or are both a weak acid and weak base present? (2) We write the appropriate chemical equation and equilibrium law. (3) We proceed with the solution.

■ **Assembling the Tools:** Since sodium is in Group 1A, that tells us that the Na^+ does not affect the pH. However the OCl^- is the conjugate base of the weak acid, HOCl. Therefore we have a solution of a weak base and we need to use K_b and the appropriate chemical reaction. The reaction we need describes how OCl^- reacts with water.

■ If you have trouble writing the correct chemical equation for this equilibrium, you should review Section 17.3.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

Then we write the appropriate equilibrium law as

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$$

We do not know the value of K_b for OCl^- but we do know that the K_a for HOCl is 3.0×10^{-8}. We will use the equation

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$$

to calculate the needed value for K_b. Now we can set up a concentration table to help us keep track of the numbers in our calculation.

■ **Solution:** We've written the balanced chemical equation above and also the equilibrium law, and we calculated K_b from the given value of K_a.

Now let's set up the concentration table. The only sources of HOCl and OH^- are the reaction of the OCl^-, so their concentrations will each increase by *x* and the concentration of OCl^- will decrease by *x*.

	H_2O + OCl^-	$\rightleftharpoons$ HOCl	+ OH^-
Initial concentrations (*M*)	0.10	0	0
Changes in concentrations (*M*)	$-x$	$+x$	$+x$
Equilibrium conc. (*M*)	$(0.10 - x) \approx 0.10$	x	x

At equilibrium, the concentrations of HOCl and OH^- are the same, *x*.

$$[HOCl] = [OH^-] = x$$

Because K_b is so small, $[OCl^-] \approx 0.10\ M$. (Once again, we expect x to be so small that we are able to use the initial concentration of the base as if it were the equilibrium concentration.) Substituting into the K_b expression gives

$$\frac{(x)(x)}{0.10 - x} \approx \frac{(x)(x)}{0.10} = 3.3 \times 10^{-7}$$

$$x = 1.8 \times 10^{-4}\ M$$

At this point we need to remember that the value of x represents the OH^- concentration, from which we can calculate the pOH and then the pH.

$$\begin{aligned} [OH^-] &= 1.8 \times 10^{-4}\ M \\ \text{pOH} &= -\log(1.8 \times 10^{-4}) = 3.74 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 3.74 \\ &= 10.26 \end{aligned}$$

The pH of this solution is 10.26.

■ **Is the Answer Reasonable?** First, we check our assumption and find it is correct $(0.10 - 0.00018 = 0.10)$. Also, from the nature of the salt, we expect the solution to be basic. The calculated pH corresponds to a basic solution, so the answer seems to be reasonable. You've also seen that we can check the accuracy of the answer by substituting the calculated equilibrium concentrations into the mass action expression.

$$\frac{[HOCl][OH^-]}{[OCl^-]} = \frac{(x)(x)}{0.10} = \frac{(1.8 \times 10^{-4})^2}{0.10} = 3.2 \times 10^{-7}$$

The result is quite close to our value of K_b, so our answers are correct.

Practice Exercises

17.27 | What is the pH of a solution when 25.0 g of methylammonium chloride, CH_3NH_3Cl, is dissolved in enough water to make 500.0 mL of solution? (*Hint:* What is the molarity of the CH_3NH_3Cl solution?)

17.28 | What is the pH of a 0.10 M solution of $NaNO_2$?

17.29 | 500.0 mL of a 0.20 M solution of ammonia is mixed with 500.0 mL of a 0.2 M solution of HBr. What is the pH of the resulting solution of NH_4Br?

Salts of a Weak Acid and a Weak Base

There are many salts whose ions are both able to affect the pH of the salt solution. Whether or not the salt has a net effect on the pH now depends on the relative strengths of both ions. If the cation and anion are identical in their respective strengths, the salt has no net effect on pH. In ammonium acetate, for example, the ammonium ion is an acidic cation and the acetate ion is a basic anion. However, the K_a of NH_4^+ is 5.6×10^{-10} and the K_b of $C_2H_3O_2^-$ just happen to be the same, 5.6×10^{-10}. The cation tends to produce H^+ ions to the same extent that the anion tends to produce OH^-. So in aqueous ammonium acetate, $[H^+] = [OH^-]$, and the solution has a pH of 7.

■ If *neither* the cation nor the anion is able to affect the pH, the salt solution will be neutral (provided no other acidic or basic solutes are present).

Now consider ammonium formate, NH_4CHO_2. The formate ion, CHO_2^-, is the conjugate base of the weak acid, formic acid, so it is a Brønsted base. Its K_b is 5.6×10^{-11}. Comparing this value to the (slightly larger) K_a of the ammonium ion, 5.6×10^{-10}, we see that NH_4^+ is slightly stronger as an acid than the formate ion is as a base. As a result, a solution of ammonium formate is slightly acidic. We are not concerned here about calculating a pH, only in predicting if the solution is acidic, basic, or neutral.

Practice Exercises

17.30 | Will an aqueous solution of ammonium cyanide, NH_4CN, be acidic, basic, or neutral? (*Hint:* These anions and cations are conjugates of an acid and a base listed in Tables 17.2 and 17.3.)

17.31 | Will an aqueous solution of ammonium nitrite, NH_4NO_2, be acidic, basic, or neutral?

17.7 | Buffer Solutions

Many chemical and biological systems are quite sensitive to pH. For example, if the pH of your blood were to change from what it should be, within the range of 7.35 to 7.42, either to 7.00 or to 8.00, you would die. Lakes and streams with a pH less than 5 often cannot support fish life. Thus, a change in pH can produce unwanted effects, and systems that are sensitive to pH must be protected from the H^+ or OH^- that might be formed or consumed by some reaction. *Buffers* are mixtures of solutes that accomplish this. Such a solution is said to be *buffered* or it is described as a *buffer solution.*

Composition of a Buffer

A **buffer** contains solutes that enable it to resist large changes in pH when small amounts of either strong acid or strong base are added to it. Ordinarily, the buffer consists of two solutes, one a weak Brønsted acid and the other its conjugate base. If the acid is molecular, then the conjugate base is *supplied by a soluble salt of the acid.* For example, a common buffer system consists of acetic acid plus sodium acetate, with the salt's acetate ion serving as the Brønsted base. In your blood, carbonic acid (H_2CO_3, a weak diprotic acid) and the bicarbonate ion (HCO_3^-, its conjugate base) serve as one of the buffer systems used to maintain a remarkably constant pH in the face of the body's production of organic acids by metabolism. Another common buffer consists of the weakly acidic cation, NH_4^+, supplied by a salt like NH_4Cl, and its conjugate base, NH_3.

One important point about buffers is the distinction between keeping a solution at a particular pH and keeping it neutral—at a pH of 7. Although it is certainly possible to buffer a solution at pH 7, buffers can be made that will work at any pH value throughout the pH scale.

How a Buffer Works

TOOLS

How buffers work

To work, a buffer must be able to neutralize either a strong acid or strong base that is added. This is precisely what the conjugate acid and base components of the buffer do. Consider, for example, a buffer composed of acetic acid, $HC_2H_3O_2$, and acetate ion, $C_2H_3O_2^-$, supplied by a salt such as $NaC_2H_3O_2$. If we add extra H^+ to the buffer (from a strong acid) the acetate ion (the weak conjugate base) can react with it as follows.

$$H^+(aq) + C_2H_3O_2^-(aq) \longrightarrow HC_2H_3O_2(aq)$$

Thus, the added H^+ changes some of the buffer's Brønsted base, $C_2H_3O_2^-$, to its conjugate (weak) acid, $HC_2H_3O_2$. This reaction prevents a large buildup of H^+ and a corresponding decrease in pH that would otherwise be caused by the addition of the strong acid.

■ Not all the added H^+ is neutralized, so the pH is lowered a little. Soon we'll see how much it changes.

A similar response occurs when a strong base is added to the buffer. The OH^- from the strong base will react with some $HC_2H_3O_2$.

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$$

Here the added OH^- changes some of the buffer's Brønsted acid, $HC_2H_3O_2$, into its conjugate base, $C_2H_3O_2^-$. This prevents a buildup of OH^-, which would otherwise cause a large increase in the pH. Thus, one member of a buffer team neutralizes H^+ that might get into the solution, and the other member neutralizes OH^-. *Understanding buffers is an important tool for chemists to use in applications ranging from the protocols of a research project to designing a consumer product.*

Practice Exercises

17.32 | Acetic acid, $HC_2H_3O_2$, and sodium acetate, $NaC_2H_3O_2$ (this provides the acetate ion $C_2H_3O_2^-$), can be used to make an "acetate" buffer. Does the acetate ion or the acetic acid increase when a strong acid is added to the buffer? Is it the acetate ion or acetic acid that decreases when a strong base is added to the buffer? Explain your answers. (*Hint:* Which of the buffer components will react with HCl? Which will react with NaOH?)

17.33 | For a buffer composed of NH_3 and NH_4^+ (from NH_4Cl), write chemical equations that show what happens when (a) a small amount of strong acid is added, and (b) a small amount of strong base is added.

Calculating the pH of a Buffer Solution

Calculating the pH of a buffer mixture follows the same procedures we employed in Section 17.5 with a few small changes. The following example illustrates the principles involved.

Example 17.6

Calculating the pH of a Buffer

To study the effects of a weakly acidic medium on the rate of corrosion of a metal alloy, a student prepared a buffer solution containing both 0.110 *M* $NaC_2H_3O_2$ and 0.090 *M* $HC_2H_3O_2$. What is the pH of this solution?

■ **Analysis:** We recognize that this is a buffer solution because it contains *both* the weak acid $HC_2H_3O_2$ and its conjugate base $C_2H_3O_2^-$. Also, earlier we noted that when both solute species are present we can use *either* K_a or K_b to perform calculations, whichever is handy.

■ **Assembling the Tools:** In our tables we find $K_a = 1.8 \times 10^{-5}$ for $HC_2H_3O_2$, so the simplest approach is to use K_a and the corresponding balanced chemical equation for the ionization of the acid.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \qquad K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

We will also be able to use the simplifying approximations developed earlier; these almost always work for buffers.

■ **Solution:** As usual, we begin with the chemical equation and the expression for K_a that we wrote above. Next, let's set up the concentration table so we can proceed logically. We will take the initial concentrations of $HC_2H_3O_2$ and $C_2H_3O_2^-$ to be the values given in the problem. There's no H^+ present from a strong acid, so we set this concentration equal to zero. If the initial concentration of H^+ is zero, its concentration must increase on the way to equilibrium, so under H^+ in the change row we enter $+x$. The other changes follow from that. For buffer solutions the quantity x will be very small, so it is safe to make the simplifying approximations in the last row. Here's the completed table.

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	$+$	$C_2H_3O_2^-$
Initial concentrations (*M*)	0.090		0		0.11
Changes in concentrations (*M*)	$-x$		$+x$		$+x$
Equilibrium concentrations (*M*)	$(0.090 - x)$ ≈ 0.090		x		$(0.11 + x)$ ≈ 0.11

What remains, then, is to substitute the quantities from the last row of the table into the K_a expression.

$$\frac{(x)(0.11 + x)}{(0.090 - x)} \approx \frac{(x)(0.11)}{(0.090)} = 1.8 \times 10^{-5}$$

Solving for x gives us

$$x = \frac{(0.090) \times 1.8 \times 10^{-5}}{(0.11)} = 1.5 \times 10^{-5}$$

Because x equals $[H^+]$, we now have $[H^+] = 1.5 \times 10^{-5}\ M$. Then we calculate pH:

$$\text{pH} = -\log(1.5 \times 10^{-5}) = 4.82$$

Thus, the pH of the buffer is 4.82.

■ Notice how small x is compared to the initial concentrations. The simplification was valid.

■ **Is the Answer Reasonable?** Again, we check our assumptions and find they worked ($0.090 - 0.000015 = 0.090$ and $0.11 + 0.000015 = 0.11$). Also, we can check the answer in the usual way by substituting our calculated equilibrium values into the mass action expression. Let's do it.

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(1.5 \times 10^{-5})(0.11)}{(0.090)} = 1.8 \times 10^{-5}$$

The reaction quotient equals K_a, so the values we've obtained are correct equilibrium concentrations.

Practice Exercises

17.34 | Calculate the pH of the buffer solution in the preceding example by using the K_b for $C_2H_3O_2^-$. Be sure to write the chemical equation for the equilibrium as the reaction of $C_2H_3O_2^-$ with water. Then use the chemical equation as a guide in setting up the equilibrium expression for K_b. (*Hint:* If you work the problem correctly, you should obtain the same answer as above.)

17.35 | One liter of buffer is made by dissolving 100.0 grams of acetic acid, $HC_2H_3O_2$, and 100.0 grams of sodium acetate, $NaC_2H_3O_2$, in enough water to make one liter. What is the pH of this solution?

The "Common Ion Effect"

If the solution in the preceding example had contained only acetic acid with a concentration of 0.090 *M*, the calculated $[H^+]$ would have been $1.3 \times 10^{-3}\ M$, considerably higher than that of the buffer, which also contains 0.11 *M* $C_2H_3O_2^-$. The effect of adding sodium acetate, a substance containing $C_2H_3O_2^-$ ion, to a solution of acetic acid is to suppress the ionization of the acid—it's an example of Le Châtelier's principle. Suppose, for example, we had established the equilibrium

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

According to Le Châtelier's principle, if we add $C_2H_3O_2^-$, the reaction will proceed in a direction to remove some of it. This will shift the equilibrium to the left, thereby reducing the concentration of H^+.

In this example, acetate ion is said to be a **common ion,** in the sense that it is *common* to both the acetic acid equilibrium and to the salt we added, sodium acetate. The suppression of the ionization of acetic acid by addition of the common ion is referred to as the **common ion effect.** We will encounter this phenomenon again in Chapter 18 when we consider the solubilities of salts.

Simplifications in Buffer Calculations

There are two useful simplifications that we can use in working buffer calculations. The first is the one we made in Example 17.3:

> Because the initial concentrations are so close to the equilibrium concentrations in the buffer mixture, we can use *initial* concentrations of both the weak acid and its conjugate base as though they were equilibrium values.

■ There are some buffer systems for which these simplifications might not work. However, you will not encounter them in this text.

A further simplification can be made because the mass action expression contains the ratio of the molar concentrations (in units of moles per liter) of the acid and conjugate base. Let's enter these units for the acid and its conjugate base into the mass action expression. For an acid HA,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](\text{mol } A^-\ \cancel{L^{-1}})}{(\text{mol } HA\ \cancel{L^{-1}})} = \frac{[H^+](\text{mol } A^-)}{(\text{mol } HA)} \tag{17.16}$$

Notice that the units L^{-1} cancel from the numerator and denominator. This means that for a given acid–base pair, $[H^+]$ is determined by the *mole* ratio of conjugate base to conjugate acid; we don't *have* to use molar concentrations.

> *For buffer solutions **only,*** we can use either molar concentrations or moles in the K_a (or K_b) expression to express the amounts of the acid and its conjugate base. However, *we must use the same units for each member of the pair.*

A further consequence of the relationship derived in Equation 17.16 is that the pH of a buffer should not change if the buffer is diluted. Dilution changes the volume of a solution but it does not change the number of moles of the solutes, so their mole *ratio* remains constant and so does $[H^+]$.

Preparing Buffers with a Desired pH

The hydrogen ion concentration of a buffer is controlled by both K_a and the ratio of concentrations (or ratio of moles) of the members of the acid–base pair. This can be seen by rearranging Equation 17.16 to solve for $[H^+]$:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{17.17}$$

or

$$[H^+] = K_a \frac{\text{mol } HA}{\text{mol } A^-} \tag{17.18}$$

Solutions of conjugate acid–base pairs will generally act as buffers when the mole (or molarity) ratio of acid to base is between 0.1 and 10. When this ratio is less than 0.1, added base will cause large pH changes. When the ratio is greater than 10, small additions of acid will cause large pH changes. When the ratio is close to 1.0, the solution will be effective if either strong acid or strong base is added. Therefore, if we want to prepare a buffer that works well near some specified pH, we look for an acid with a K_a as close to the desired pH as possible. A high concentration of both the conjugate acid and base will increase the buffer's ability to resist pH change. This is called the **buffer capacity,** and it is equal to the moles of strong acid, or strong base, needed to change the pH of one liter of buffer by 1.0 pH unit. For experiments in biology, the toxicity of the members of the acid–base pair must also be considered, and that often narrows the choices considerably.

Example 17.7

Preparing a Buffer Solution to Have a Predetermined pH

A solution buffered at a pH of 5.00 is needed in an experiment. Can we use acetic acid and sodium acetate to make it? If so, what is the mole ratio of acetic acid and sodium acetate that will result in a pH = 5.00 solution? How many moles of $NaC_2H_3O_2$ must be added to 1.0 L of a solution that contains 1.0 mol $HC_2H_3O_2$ to prepare the buffer?

Analysis: We need to do three things in this problem. First, we need to decide if, in fact, acetic acid can be used for a pH = 5.00 buffer. Second, we need to use the appropriate equations to determine the mole ratio and then, third, the amount of sodium acetate to use.

Assembling the Tools: The first tool describes the necessary relationship between pK_a and pH to successfully prepare a buffer solution:

$$\text{pH} = \text{p}K_a \pm 1$$

If we only have the K_a we also need Equation 17.6 to calculate the pK_a. Next we need the equations to convert pH to $[H^+]$ and then use it to solve Equation 17.16 to calculate the necessary mole ratio. Once we have this, we can proceed to calculate the number of moles of $C_2H_3O_2^-$ needed, and then the number of moles of $NaC_2H_3O_2$.

Solution: Looking up the K_a for acetic acid we find it is 1.8×10^{-5}. Because we want the pH to be 5.00, the pK_a of the selected acid should be 5.00 ± 1. We use Equation 17.6 to calculate the pK_a.

$$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

From this we determine that acetic acid *is appropriate* for this buffer.

Next, we use Equation 17.16 to find the mole ratio of solutes.

$$[\text{H}^+] = K_a \times \frac{(\text{mol HC}_2\text{H}_3\text{O}_2)}{(\text{mol C}_2\text{H}_3\text{O}_2^-)}$$

First, let's solve for the mole ratio.

$$\frac{(\text{mol HC}_2\text{H}_3\text{O}_2)}{(\text{mol C}_2\text{H}_3\text{O}_2^-)} = \frac{[\text{H}^+]}{K_a}$$

The desired pH = 5.00, so $[H^+] = 1.0 \times 10^{-5}$; also $K_a = 1.8 \times 10^{-5}$. Substituting gives

$$\frac{(\text{mol HC}_2\text{H}_3\text{O}_2)}{(\text{mol C}_2\text{H}_3\text{O}_2^-)} = \frac{1.0 \times 10^{-5}}{1.8 \times 10^{-5}} = 0.56$$

This is the *mole* ratio of the buffer components that is needed.

For the final step, the solution we are preparing contains 1.0 mol $HC_2H_3O_2$, so the number of moles of acetate ion required is

$$\begin{aligned}\text{moles C}_2\text{H}_3\text{O}_2^- &= \frac{1.0 \text{ mol HC}_2\text{H}_3\text{O}_2}{0.56} \\ &= 1.8 \text{ mol C}_2\text{H}_3\text{O}_2^-\end{aligned}$$

For each mole of $NaC_2H_3O_2$ there is one mole of $C_2H_3O_2^-$, so to prepare the solution we need 1.8 mol $NaC_2H_3O_2$.

Are the Answers Reasonable? A 1-to-1 mole ratio of $C_2H_3O_2^-$ to $HC_2H_3O_2$ would give pH = pK_a = 4.74. The desired pH of 5.00 is slightly more basic than 4.74, so can expect that the amount of conjugate base needed should be larger than the amount of conjugate acid. Our answer of 1.8 mol of $NaC_2H_3O_2$ appears to be reasonable.

Practice Exercises

17.36 | From Table 17.2 select an acid that, along with its sodium salt, can be used to make a buffer that has a pH of 5.25. If you have 500.0 mL of a 0.200 *M* solution of that acid, how many grams of the corresponding sodium salt do you have to dissolve to obtain the desired pH? (*Hint:* There is more than one correct answer to this problem. The first step is to determine the ratio of molarities of the conjugate acid and conjugate base.)

17.37 | A chemist needed an aqueous buffer with a pH of 3.90. Would formic acid and its salt, sodium formate, make a good pair for this purpose? If so, what mole ratio of the acid, $HCHO_2$, to the anion of this salt, CHO_2^-, is needed? How many grams of $NaCHO_2$ would have to be added to a solution that contains 0.10 mol $HCHO_2$?

If you take a biology course, you're likely to run into a logarithmic form of Equation 17.9 called the **Henderson–Hasselbalch equation**. This is obtained by taking the negative logarithm of both sides of Equation 17.9 and rearranging to get

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} \tag{17.19}$$

In most buffers used in the life sciences, the anion A^- comes from a salt in which the cation has a charge of 1+, such as Na*A*, and the acid is monoprotic. With these as conditions, the equation is sometimes written

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]} \tag{17.20}$$

For practice, you may wish to apply this equation to buffer problems at the end of the chapter.

Calculating pH Change for a Buffer

Earlier we described how a buffer is able to neutralize small amounts of either strong acid or base to keep the pH from changing by large amounts. We can use this knowledge now to calculate how much the pH will change.

Example 17.8

Calculating How a Buffer Resists Changes in pH

How much will the pH change if 0.020 mol of HCl is added to a buffer solution that was made by dissolving 0.12 mol of NH_3 and 0.095 mol of NH_4Cl in 250 mL of water?

Analysis: This problem will require two calculations. The first is to determine the pH of the original buffer. The second is to determine the pH of the mixture after the HCl has been added. For the second calculation, we have to determine how the acid changes the amounts of NH_3 and NH_4^+.

Assembling the Tools: For the pH of the initial solution we need the chemical reaction and the K_b for NH_3.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

To determine the pH of the solution after the HCl was added we need the chemical reaction for HCl in this mixture. Since HCl is a strong acid, it will react quantitatively (completely) with the conjugate base of the buffer—in this case, NH_3. The balanced molecular equation is

$$NH_3 + HCl \longrightarrow NH_4Cl$$

In this case it is better to write the net ionic equation as

$$NH_3 + H^+ \longrightarrow NH_4^+$$

We then do a limiting reactant calculation to determine how much of the NH_3 will be converted to NH_4^+. We then use the new amounts of NH_3 and NH_4^+ to determine the pH.

■ **Solution:** We begin by calculating the pH of the buffer before the HCl is added. The solution contains 0.12 mol of NH_3 and 0.095 mol of NH_4^+ from the complete dissociation of the salt NH_4Cl. We can enter these quantities into the mass action expression in place of concentrations and solve for $[OH^-]$. As noted earlier, we can use moles of NH_3 and NH_4^+ in place of molarities to solve buffer problems.

■ The solution also contains 0.095 mol of Cl^-, of course, but this ion is not involved in the equilibrium.

$$1.8 \times 10^{-5} = \frac{(\text{mol } NH_4^+) \times [OH^-]}{(\text{mol } NH_3)} = \frac{(0.095)[OH^-]}{(0.12)}$$

solving for $[OH^-]$ gives

$$[OH^-] = 2.3 \times 10^{-5}$$

To calculate the pH, we obtain pOH and subtract it from 14.00.

$$\text{pOH} = -\log(2.3 \times 10^{-5}) = 4.64$$
$$\text{pH} = 14.00 - 4.64 = 9.36$$

This is the pH before we add any HCl.

Next, we consider the reaction that takes place when we add the HCl to the buffer. The 0.020 mol of HCl is completely ionized, so we're adding 0.020 mol H^+. The 0.020 mol of acid will react with 0.020 mol of NH_3 to form 0.020 mol of NH_4^+. This causes the number of moles of NH_3 to *decrease* by 0.020 mol and the number of moles of NH_4^+ to *increase* by 0.020 mol. After addition of the acid, we have

■ The equilibrium constant for this reaction is 1.8×10^{10}, so the reaction goes almost to completion. Nearly all the added H^+ reacts with NH_3.

$$\text{moles of } NH_3 = \overset{\substack{\text{Number of moles}\\ \text{in the original}\\ \text{buffer mixture}\\ \searrow}}{0.12 \text{ mol}} - \overset{\substack{\text{Change in the}\\ \text{number of moles}\\ \text{because of reaction}\\ \swarrow}}{0.020 \text{ mol}} = 0.10 \text{ mol } NH_3$$

$$\text{moles of } NH_4^+ = 0.095 \text{ mol} + 0.020 \text{ mol} = 0.115 \text{ mol } NH_4^+$$

We now use these new amounts of NH_3 and NH_4^+ to calculate the new pH of the buffer solution. First, we calculate $[OH^-]$.

$$1.8 \times 10^{-5} = \frac{(\text{mol } NH_4^+) \times [OH^-]}{(\text{mol } NH_3)} = \frac{(0.115)[OH^-]}{(0.10)}$$

Solving for $[OH^-]$ gives

$$[OH^-] = 1.6 \times 10^{-5}$$

To calculate the pH, we obtain pOH and subtract it from 14.00.

$$\text{pOH} = -\log(1.6 \times 10^{-5}) = 4.80$$
$$\text{pH} = 14.00 - 4.80 = 9.20$$

This is the pH after addition of the acid. We're asked for the change in pH, so we take the difference between the two values:

$$\text{change in pH} = 9.20 - 9.36 = -0.16$$

Thus, the pH has decreased by 0.16 pH units.

■ **Is the Answer Reasonable?** In general, we can assume that changes in pH should be small (less than 1.0 pH unit), otherwise there's no simple way to estimate how *much* the pH will change when H^+ or OH^- is added to the buffer. However, we can anticipate the *direction* of the change. Adding H^+ to a buffer will lower the pH somewhat and adding OH^- will raise it. In this example, the buffer is absorbing H^+, so its pH should decrease, and our calculations agree. If our calculated pH had been higher than the original, we might expect to find errors in the calculation of the final values for the number of moles of NH_3 and NH_4^+.

Practice Exercises

17.38 | How much will the pH change if we add 0.15 mol NaOH to 1.00 L of a buffer that contains 1.00 mol $HC_2H_3O_2$ and 1.00 mol $NaC_2H_3O_2$? (*Hint:* Will the NaOH react with $HC_2H_3O_2$ or $NaC_2H_3O_2$? Write the equation for the reaction.)

17.39 | A buffer is prepared by mixing 50.0 g of NH_3 and 50.0 g of NH_4Cl in 0.500 L of solution. What is the pH of this buffer, and what will the pH change to if 5.00 g of HCl is then added to the mixture?

If you look back over the calculations in the preceding example, you can get some feel for how effective buffers can be at preventing large swings in pH. Notice that we've added enough HCl to react with approximately 20% of the NH_3 in the solution, but the pH changed by only 0.16 pH units. If we were to add this same amount of HCl to 0.250 L of pure water, it would give a solution with $[H^+] = 0.080\ M$. Such a solution would have a pH of 1.10, which is quite acidic. However, the buffer mixture stayed basic, with a pH of 9.20, even after addition of the acid. That's pretty remarkable!

17.8 | Polyprotic Acids

Until now our discussion of weak acids has focused entirely on equilibria involving monoprotic acids. There are, of course, many acids capable of supplying more than one H^+ per molecule. Recall that these are called polyprotic acids. Examples include sulfuric acid, H_2SO_4, carbonic acid, H_2CO_3, and phosphoric acid, H_3PO_4. These acids undergo ionization in a series of steps, each of which releases one proton. For weak polyprotic acids, such as H_2CO_3 and H_3PO_4, each step is an equilibrium. Even sulfuric acid, which we consider a strong acid, is not completely ionized. Loss of the first proton to yield the HSO_4^- ion is complete, but the loss of the second proton is incomplete and involves an equilibrium. In this section, we will focus our attention on weak polyprotic acids as well as solutions of their salts.

Vitamin C. Many fruits and vegetables contain ascorbic acid (vitamin C), a weak diprotic acid with the formula $H_2C_6H_6O_6$. *(Andy Washnik)*

Polyprotic acids ionize stepwise

Let's begin with the weak diprotic acid, H_2CO_3. In water, the acid ionizes in two steps, each of which is an equilibrium that transfers an H^+ ion to a water molecule.

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$
$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

As usual, we can use H^+ in place of H_3O^+ and simplify these equations to give

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

Each step has its own ionization constant, K_a, which we identify as K_{a_1} for the first step and K_{a_2} for the second. For carbonic acid,

$$K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

Notice that each ionization makes a contribution to the total molar concentration of H^+, and one of our goals here is to relate the K_a values and the concentration of the acid to [H$^+$]. At first glance, this seems to be a formidable task, but certain simplifications are justified that make the problem relatively simple to solve.

Simplifications in Calculations

The principal factor that simplifies calculations involving many polyprotic acids is the large differences between successive ionization constants. Notice that for H_2CO_3, K_{a_1} is much larger than K_{a_2} (they differ by a factor of nearly 10,000). Similar differences between K_{a_1} and K_{a_2} are observed for many diprotic acids. One reason is that an H^+ is lost much more easily from the neutral H_2A molecule than from the HA^- ion. The stronger attraction of the opposite charges inhibits the second ionization. Typically, K_{a_1} is greater than K_{a_2} by a factor of between 10^4 and 10^5, as the data in Table 17.4 show. For a triprotic acid, such as phosphoric acid, H_3PO_4, the second acid ionization constant is similarly greater than the third.

■ Additional K_a values of polyprotic acids are located in Appendix C–7.

Because K_{a_1} is so much larger than K_{a_2}, at equilibrium virtually all the H^+ in a solution of the acid comes from the first step in the ionization. In other words,

$$[H^+]_{\text{equilib}} = [H^+]_{\text{first step}} + [H^+]_{\text{second step}}$$

$$[H^+]_{\text{first step}} \gg [H^+]_{\text{second step}}$$

Therefore, we make the approximation that

$$[H^+]_{\text{equilib}} \approx [H^+]_{\text{first step}}$$

This means that as far as calculating the H^+ concentration is concerned, we can treat the acid as though it were a monoprotic acid and ignore the second step in the ionization. In addition we have

$$[HCO_3{}^-]_{\text{equilib}} = [HCO_3{}^-]_{\text{first step}} - [CO_3{}^{2-}]_{\text{second step}}$$

However, since $[CO_3{}^{2-}]_{\text{second step}} = [H^+]_{\text{second step}}$ and $[H^+]_{\text{second step}}$ is very small we can say that

$$[HCO_3{}^-]_{\text{equilib}} \approx [HCO_3{}^-]_{\text{first step}}$$

Table 17.4 Acid Ionization Constants for Polyprotic Acids

		Acid Ionization Constant for Successive Ionizations (25 °C)		
Name	**Formula**	**1st**	**2nd**	**3rd**
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Hydrosulfuric acid	H_2S (*aq*)	8.9×10^{-8}	1×10^{-19}	
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Arsenic acid	H_3AsO_4	5.5×10^{-3}	1.7×10^{-7}	5.1×10^{-12}
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Selenic acid	H_2SeO_4	Large	1.2×10^{-2}	
Telluric acid	H_6TeO_6	2×10^{-8}	1×10^{-11}	
Sulfurous acid	H_2SO_3	1.2×10^{-2}	6.6×10^{-8}	
Selenous acid	H_2SeO_3	4.5×10^{-3}	5×10^{-8}	
Tellurous acid	H_2TeO_3	3.3×10^{-3}	2.0×10^{-8}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Oxalic acid	$H_2C_2O_4$	6.0×10^{-2}	6.1×10^{-5}	
Citric acid (18 °C)	$H_3C_6H_5O_7$	7.1×10^{-4}	1.7×10^{-5}	6.3×10^{-6}

It is therefore reasonable to conclude that

$$[\mathrm{H^+}]_{\mathrm{equilib}} = [\mathrm{HCO_3^-}]_{\mathrm{equilib}}$$

This last equality leads to the interesting result

$$K_{a_2} = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 5.6 \times 10^{-11} = [\mathrm{CO_3^{2-}}]$$

meaning the molar concentration of the carbonate ion is simply K_{a_2} when the only solute is carbonic acid. This will be true for other diprotic acids that have widely different K_{a_1} and K_{a_2} values.

Example 17.9 illustrates how these relationships are applied.

Example 17.9
Calculating the Concentrations of Solute Species in a Solution of a Polyprotic Acid

Calculate the concentrations of all the species in a solution of 0.040 *M* $\mathrm{H_2CO_3}$ as well as the pH of the solution.

■ **Analysis:** We will use the procedures developed above to determine $[\mathrm{H^+}]$, pH, $[\mathrm{H_2CO_3}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$.

■ **Assembling the Tools:** As in any equilibrium problem, we begin with the chemical equations and the K_a expressions

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-} \qquad K_{a_1} = \frac{[\mathrm{H^+}][\mathrm{CO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}} \qquad K_{a_2} = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 5.6 \times 10^{-11}$$

Once we have these equations, it is a matter of applying them, with our chemical insights, in the appropriate manner. The two approximations that will be very useful are

$$[\mathrm{H^+}]_{\mathrm{equilib}} \approx [\mathrm{H^+}]_{\text{first step}}$$

and

$$[\mathrm{HCO_3^-}]_{\mathrm{equilib}} \approx [\mathrm{HCO_3^-}]_{\text{formed in first step}}$$

■ **Solution:** Treating $\mathrm{H_2CO_3}$ as though it were a monoprotic acid yields a problem similar to Example 17.3. We know some of the $\mathrm{H_2CO_3}$ ionizes; let's call this amount *x*. If *x* moles per liter of $\mathrm{H_2CO_3}$ ionizes, then *x* moles per liter of $\mathrm{H^+}$ and $\mathrm{HCO_3^-}$ are formed, and the concentration of $\mathrm{H_2CO_3}$ is reduced by *x*.

	$\mathrm{H_2CO_3}$	$\rightleftharpoons$	$\mathrm{H^+}$	+	$\mathrm{HCO_3^-}$
Initial concentrations (*M*)	0.040		0		0
Changes in concentrations (*M*)	$-x$		$+x$		$+x$
Equilibrium concentrations (*M*)	$(0.040 - x) \approx 0.040$		x		x

Substituting into the expression for K_{a_1} gives

$$\frac{x^2}{(0.040 - x)} \approx \frac{x^2}{0.040} = 4.3 \times 10^{-7}$$

Solving for *x* gives $x = 1.3 \times 10^{-4}$, so $[\mathrm{H^+}] = [\mathrm{HCO_3^-}] = 1.3 \times 10^{-4}$ *M*. Notice that our simplifying assumption is true and $[\mathrm{H_2CO_3}]$ remains at 0.040 *M*. From this we can now calculate the pH.

$$\mathrm{pH} = -\log(1.3 \times 10^{-4}) = 3.89$$

Now let's calculate the concentration of CO_3^{2-}. We obtain this from the expression for K_{a_2}.

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

■ Keep in mind that for a given solution, the values of H^+ used in the expressions for K_{a_1} and K_{a_2} are identical. At equilibrium there is only *one* equilibrium H^+ concentration.

In our analysis, we concluded that we can use the approximations

$$[H^+]_{\text{equilib}} \approx [H^+]_{\text{first step}}$$
$$[HCO_3^-]_{\text{equilib}} \approx [HCO_3^-]_{\text{first step}}$$

Substituting the values obtained above gives us

$$\frac{(\cancel{1.3 \times 10^{-4}})[CO_3^{2-}]}{\cancel{1.3 \times 10^{-4}}} = 5.6 \times 10^{-11}$$

$$[CO_3^{2-}] = 5.6 \times 10^{-11} = K_{a_2}$$

Let's summarize the results. At equilibrium, we have

$$[H_2CO_3] = 0.040\ M$$
$$[H^+] = [HCO_3^-] = 1.3 \times 10^{-4}\ M \text{ and pH} = 3.89$$
$$[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$$

■ **Are the Answers Reasonable?** To start, we check our assumptions. First, the initial concentration was assumed to be much larger than the hydrogen ion concentration, and it is $(0.040 - 0.00013 = 0.040)$. The second approximation was that the amount of CO_3^{2-} formed would be very small in relation to the HCO_3^- (and also H^+) concentration calculated in the first step. This assumption is true too $(1.3 \times 10^{-4} - 5.6 \times 10^{-11} = 1.3 \times 10^{-4})$. We can also check that the hydrogen ions added in the second step are inconsequential $(1.3 \times 10^{-4} + 5.6 \times 10^{-11} = 1.3 \times 10^{-4})$.

We've checked our assumptions and they are okay. The pH is less than 7; this is what we expect from an acid. If more verification is needed, you can always perform a quick check of the answers by substituting them into the appropriate mass action expressions:

$$\frac{(1.3 \times 10^{-4})(1.3 \times 10^{-4})}{0.040} = 4.2 \times 10^{-7}, \quad \text{which is very close to } K_{a_1}$$

$$\frac{(1.3 \times 10^{-4})(4.7 \times 10^{-11})}{(1.3 \times 10^{-4})} = 5.6 \times 10^{-11}, \quad \text{which equals } K_{a_2}$$

One last thing: the problem asked for *all species* in this solution of H_2CO_3. Two other substances are in the reaction mixture, water and hydroxide ions and a rigorous solution would also include these species.

Practice Exercises

17.40 | Write the three ionization steps for phosphoric acid, H_3PO_4, and write the K_a expressions for each step. (*Hint:* Recall that one proton is ionized in each step.)

17.41 | Ascorbic acid (vitamin C) is a diprotic acid, $H_2C_6H_6O_6$. (See Table 17.4.) Calculate $[H^+]$, pH, and $[C_6H_6O_6^{2-}]$ in a 0.10 M solution of ascorbic acid.

One of the most interesting observations we can derive from the preceding example is that *in a solution that contains a polyprotic acid* ***as the only solute,*** *the concentration of the ion formed in the second step of the ionization equals* K_{a_2}.

Salts of Polyprotic Acids

You learned earlier that the pH of a salt solution is controlled by whether the salt's cation, anion, or both are able to react with water. For simplicity, the salts of polyprotic acids that we will discuss here will be limited to those containing *nonacidic* cations, such as sodium or potassium ion. In other words, we will study salts in which the anion alone is basic and thereby affects the pH of a solution.

A typical example of a salt of a polyprotic acid is sodium carbonate, Na_2CO_3. It is a salt of H_2CO_3, and the salt's carbonate ion is a Brønsted base that is responsible for *two* equilibria that furnish OH^- ion and thereby affect the pH of the solution. These equilibria and their corresponding expressions for K_b are as follows:

$$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad \textbf{(17.21)}$$

$$K_{b_1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

$$HCO_3^-(aq) + H_2O \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \qquad \textbf{(17.22)}$$

$$K_{b_2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$

The calculations required to determine the concentrations of the species involved in these equilibria are very much like those involving weak diprotic acids. The difference is that the chemical reactions here are those of bases instead of acids. In fact, *the simplifying assumptions in our calculations will be almost identical to those for weak polyprotic acids.*

First, let's determine the value of K_{b_1} and K_{b_2} for the successive equilibria in Equations 17.21 and 17.22. To obtain these constants, we will use the relationship that $K_a \times K_b = K_w$ along with the tabulated values of K_{a_1} and K_{a_2} for H_2CO_3.

At the start of this section we saw that $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$ are associated with K_{a_2}. When a salt containing CO_3^{2-} reacts with water, the CO_3^{2-} is the base (Equation 17.21), the conjugate acid is HCO_3^-. Therefore, K_{b_1} contains the same conjugate acid–base pair as K_{a_2}. Therefore we calculate K_{b_1} from K_{a_2} as

$$K_{b_1} = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$$

Similarly, we see that $H_2CO_3(aq)$ and $HCO_3^-(aq)$ are associated with K_{a_1}. When HCO_3^- is the base (Equation 17.22), the conjugate acid is H_2CO_3. Therefore, to calculate K_{b_2} we must use K_{a_1} because both have the same conjugate acid–base pair in the equilibrium expression

$$K_{b_2} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Now we can compare the two K_b values. For CO_3^{2-}, $K_{b_1} = 1.8 \times 10^{-4}$, and for the (much) weaker base, HCO_3^-, K_{b_2} is 2.3×10^{-8}. Thus CO_3^{2-} has a K_b nearly 10,000 times that of HCO_3^-. This means that the reaction of CO_3^{2-} with water (Equation 17.21) generates far more OH^- than the reaction of HCO_3^- (Equation 17.22). The contribution of the latter to the total pool of OH^- is relatively so small that we can safely ignore it. The simplification here is very much the same as in our treatment of the ionization of weak polyprotic acids.

$$[OH^-]_{\text{equilib}} = [OH^-]_{\text{formed in first step}} + [OH^-]_{\text{formed in second step}}$$

$$[OH^-]_{\text{formed in first step}} \gg [OH^-]_{\text{formed in second step}}$$

$$[OH^-]_{\text{equilib}} \approx [OH^-]_{\text{formed in first step}}$$

Thus, if we wish to calculate the pH of a solution of a basic anion of a polyprotic acid, *we may work exclusively with* K_{b_1} *and ignore any further reactions.* Let's study an example of how this works.

SAVOGRAN
TSP
Trisodium Phosphate
All-purpose
Heavy duty cleaner

The salt Na_3PO_4 is sold under the name trisodium phosphate or TSP. Solutions of the salt in water are quite basic and are used as an aid in cleaning grime from painted surfaces. Some states restrict the sale of TSP because the phosphate ion it contains presents a pollution problem by promoting the growth of algae in lakes. *(© 1999 Richard Megna/Fundamental Photographs)*

■ In general, K_b values for anions of polyprotic acids are not tabulated. When needed, they are calculated from the appropriate K_a values for the acids.

■ Remember: K_{b_1} comes from K_{a_2}, and K_{b_2} comes from K_{a_1}.

Example 17.10
Calculating the pH of a Solution of a Salt of a Weak Diprotic Acid

Some detergents that use sodium carbonate as their caustic ingredient. Detergents are best able to dissolve grease and grime if their solutions are basic. In these products, the basic ingredient is sodium carbonate. The salt Na_2CO_3 is relatively nontoxic and the carbonate ion it contains is a relatively strong base. The carbonate ion also serves as a water softener by precipitating Ca^{2+} ions as insoluble $CaCO_3$. *(Paul Silverman/Fundamental Photographs)*

What is the pH of a 0.11 *M* solution of Na_2CO_3?

Analysis: Based on the discussion above we will approach this question in the same way that we solved Example 17.5 previously for a salt of a monoprotic acid.

Assembling the Tools: We can ignore the reaction of HCO_3^- with water, so the only relevant equilibrium is

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad K_{b_1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 1.8 \times 10^{-4}$$

(The value of K_{b_1} was calculated from K_{a_2} in the discussion preceding this example.)

Solution: Some of the CO_3^{2-} will react; we'll let this be *x* mol L^{-1}. The concentration table, with our simplifying assumption, is as follows.

	H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
Initial concentrations (*M*)			0.11		0		0
Changes in concentrations (*M*)			$-x$		$+x$		$+x$
Equilibrium concentrations (*M*)			$(0.11 - x) \approx 0.11$		x		x

Now we're ready to insert the values in the last row of the table into the equilibrium expression for the carbonate ion.

$$\frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{(x)(x)}{0.11 - x} \approx \frac{(x)(x)}{0.11} = 1.8 \times 10^{-4}$$

$$x = [OH^-] = 4.4 \times 10^{-3} \text{ mol L}^{-1}$$

and

$$pOH = -\log (4.4 \times 10^{-3}) = 2.36$$

Finally, we calculate the pH by subtracting pOH from 14.00.

$$pH = 14.00 - 2.36 = 11.64$$

Thus, the pH of 0.11 *M* Na_2CO_3 is calculated to be 11.64. Once again we see that an aqueous solution of a salt composed of a basic anion and a neutral cation is basic.

Is the Answer Reasonable? Our result was reasonable since our assumption was true: $(0.11 - 0.0048 = 0.11)$ when properly rounded. Also, the pH we obtained corresponds to a basic solution, which is what we expect when the anion of the salt reacts as a weak base. The answer seems reasonable.

Practice Exercises

17.42 | Sodium bicarbonate gives solutions that are slightly alkaline (approximately pH 8.3), and similar solutions of sodium hydroxide (lye) are very basic with a pH around 12 or more. Lye will cause major damage, if not death, if swallowed, while sodium bicarbonate is a common antacid. Calculate the pH of a 0.10 *M* sodium carbonate solution and decide if it is an acceptable substitute for sodium bicarbonate. (*Hint:* The conjugate base in this problem is the carbonate ion.)

17.43 | What is the pH of a 0.20 *M* solution of Na_2SO_3 at 25 °C? For the diprotic acid, H_2SO_3, $K_{a_1} = 1.2 \times 10^{-2}$ and $K_{a_2} = 6.6 \times 10^{-8}$.

17.44 | Reasoning by analogy from what you learned about solutions of weak polyprotic acids, what is the molar concentration of H_2SO_3 in a 0.010 *M* solution of Na_2SO_3?

17.9 | Acid–Base Titrations

In Chapter 5 we studied the overall procedure for an acid–base titration, and we saw how titration data can be used in various stoichiometric calculations. In performing this procedure, the titration is halted at the **end point** when a change in color of an **indicator** occurs. Ideally, this end point should coincide with the theoretical **equivalence point,** where the calculated, stoichiometrically equivalent, amounts of acid and base have combined. To obtain this ideal result, selecting an appropriate indicator requires foresight. We will understand this better by studying how the pH of the solution being titrated changes with the addition of titrant.

When the pH of a solution at different stages of a titration is plotted against the volume of titrant added, we obtain a **titration curve**. The values of pH in these plots can be experimentally measured using a pH meter during the titration, or they can be calculated by the procedures we will describe below.

■ The *titrant* is the solution being slowly added from a buret to a solution in the receiving flask.

We will use the calculation method, and also demonstrate that all titration curves can be described by four calculations. Two calculations describe single points on the curve, the starting point and the equivalence point. The other two calculations are simple limiting reactant calculations for (a) mixtures between the start and the equivalence point and for (b) after the equivalence point.

TOOLS

Titration curves have four regions

Strong Acid–Strong Base Titrations

■ Not all acid–base reactions react the acid and base in a 1:1 ratio. We must always base our calculations on a balanced chemical equation.

The titration of HCl(*aq*) with a standardized NaOH solution illustrates the titration of a strong acid by a strong base. The molecular and net ionic equations are

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}$$
$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}$$

An acid–base titration. Phenolphthalein is often used as an indicator to detect the end point. *(Peter Lerman)*

Let's consider what happens to the pH of a solution, initially 25.00 mL of 0.2000 *M* HCl, as small amounts of the titrant, 0.2000 *M* NaOH, are added. We will calculate the pH of the resulting solution at various stages of the titration, retaining only two decimal places, and plot the values against the volume of titrant.

At the start, before any titrant has been added, the receiving flask contains only 0.2000 *M* HCl. Because this is a strong acid, we know that

$$[\mathrm{H^+}] = [\mathrm{HCl}] = 0.2000\ M$$

So the initial pH is

$$\mathrm{pH} = -\log(0.2000) = 0.70$$

After the start but before the equivalence point we need to determine the concentration of the excess reactant in a simple limiting reactant problem. Let's first calculate the amount of HCl initially present in 25.00 mL of 0.2000 *M* HCl.

$$25.00\ \cancel{\text{mL HCl}}\text{ soln} \times \frac{0.2000\text{ mol HCl}}{1000\ \cancel{\text{mL HCl}}\text{ soln}} = 5.000 \times 10^{-3}\text{ mol HCl}$$

Now suppose we add 10.00 mL of 0.2000 *M* NaOH from the buret. The amount of NaOH added is

$$10.00\ \cancel{\text{mL NaOH}}\text{ soln} \times \frac{0.2000\text{ mol NaOH}}{1000\ \cancel{\text{mL NaOH}}\text{ soln}} = 2.000 \times 10^{-3}\text{ mol NaOH}$$

■ Despite the high precision assumed for the molarity and the volume of the titrant, we will retain only two significant figures in the calculated pH. Precision higher than this is hard to obtain and seldom sought in actual lab work.

We can see that we have more moles of HCl than NaOH (and the mole ratio in the chemical equation is 1:1) so that the base neutralizes 2.000×10^{-3} mol of HCl, and the amount of HCl remaining is

$$(5.000 \times 10^{-3} - 2.000 \times 10^{-3})\text{ mol HCl} = 3.000 \times 10^{-3}\text{ mol HCl remaining}$$

To obtain the concentration we divide by the total volume of the solution that is now 25.00 mL + 10.00 mL = 35.00 mL = 0.03500 L. The $[H^+]$ is

■ $[H^+] = \dfrac{M_AV_A - M_BV_B}{V_A + V_B}$

$$[H^+] = \frac{3.000 \times 10^{-3}\ \text{mol}}{0.03500\ \text{L}} = 8.571 \times 10^{-2}\ M$$

The corresponding pH is 1.07.

We can repeat this calculation for as many different volumes as we care to choose as long as the volume of NaOH is less than the equivalence point volume. A spreadsheet will allow us to quickly calculate the pH of large numbers of data points, but only a few are needed to see the nature of the curve.

At the equivalence point we can calculate the volume of NaOH added as

$$\begin{aligned} M_{\text{HCl}} \times V_{\text{HCl}} &= M_{\text{NaOH}} \times V_{\text{NaOH}} \\ V_{\text{NaOH}}(\text{at eq pt}) &= \frac{(0.2000\ M_{\text{HCl}})(25.00\ \text{mL HCl})}{(0.2000\ M_{\text{NaOH}})} \\ &= 25.00\ \text{mL} \end{aligned}$$

■ The pH, at the equivalence point, of all strong acid–strong base titrations is 7.00.

■ $[OH^-] = \dfrac{M_BV_B - M_AV_A}{V_A + V_B}$

At this point we have exactly neutralized all of the acid with base and neither HCl nor NaOH are in excess. The solution contains only NaCl, and we have already observed that NaCl solutions are neutral with a pH = 7.00. The pH at the equivalence point of all strong acid–strong base titrations is 7.00.

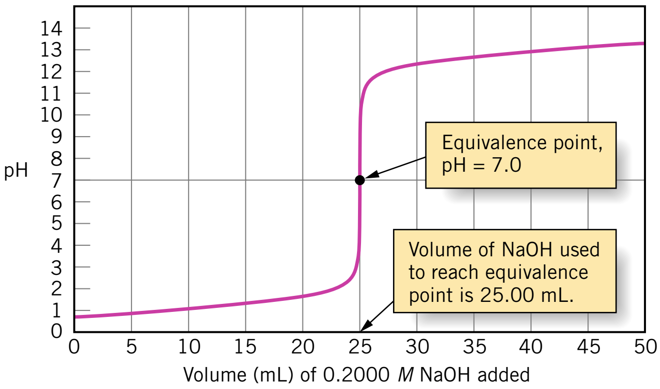
After the equivalence point we will have an excess of base. As we did before, we calculate the moles of acid and the moles of base. Now the moles of base will be larger, and we subtract the moles of acid to find the excess moles of base. This is divided by the total volume to obtain the $[OH^-]$ from which the pH is calculated.

Table 17.5 shows the results of calculating the pH of the solution in the receiving flask after the addition of further small volumes of the titrant. Figure 17.7 shows a plot of the pH of the solution in the receiving flask versus the volume of the 0.2000 *M* NaOH solution added—the *titration curve* for the titration of a strong acid with a strong base. Notice how the pH of the solution increases slowly in a linear fashion until we are very close to the equivalence point, pH = 7.00. With the addition of a very small amount of base, the

Table 17.5 **Titration of a Strong Acid with a Strong Base. The sample is 25.00 mL of 0.2000 *M* HCl and the titrant is 0.2000 *M* NaOH**

Initial Volume of HCl (mL)	Initial Amount of HCl (mol)	Volume of NaOH Added (mL)	Amount of NaOH (mol)	Amount of Excess Reagent (mol)	Total Volume of Solution (mL)	Molarity of Ion in Excess (mol L^{-1})	pH
25.00	5.000×10^{-3}	0	0	5.000×10^{-3} (H^+)	25.00	0.2000 (H^+)	0.70
25.00	5.000×10^{-3}	10.00	2.000×10^{-3}	3.000×10^{-3} (H^+)	35.00	8.571×10^{-2} (H^+)	1.07
25.00	5.000×10^{-3}	20.00	4.000×10^{-3}	1.000×10^{-3} (H^+)	45.00	2.222×10^{-2} (H^+)	1.65
25.00	5.000×10^{-3}	24.00	4.800×10^{-3}	2.000×10^{-4} (H^+)	49.00	4.082×10^{-3} (H^+)	2.39
25.00	5.000×10^{-3}	24.90	4.980×10^{-3}	2.000×10^{-5} (H^+)	49.90	4.000×10^{-4} (H^+)	3.40
25.00	5.000×10^{-3}	24.99	4.998×10^{-3}	2.000×10^{-6} (H^+)	49.99	4.000×10^{-5} (H^+)	4.40
25.00	5.000×10^{-3}	25.00	5.000×10^{-3}	0	50.00	0	7.00
25.00	5.000×10^{-3}	25.01	5.002×10^{-3}	2.000×10^{-6} (OH^-)	50.01	3.999×10^{-5} (OH^-)	9.60
25.00	5.000×10^{-3}	25.10	5.020×10^{-3}	2.000×10^{-5} (OH^-)	50.10	3.992×10^{-4} (OH^-)	10.60
25.00	5.000×10^{-3}	26.00	5.200×10^{-3}	2.000×10^{-4} (OH^-)	51.00	3.922×10^{-3} (OH^-)	11.59
25.00	5.000×10^{-3}	50.00	1.000×10^{-2}	5.000×10^{-3} (OH^-)	75.00	6.667×10^{-2} (OH^-)	12.82

curve rises very sharply and then, almost as suddenly, bends to reflect just a gradual increase in pH.



Equivalence point, pH = 7.0

Volume of NaOH used to reach equivalence point is 25.00 mL.

Figure 17.7 | **Titration curve for titrating a strong acid with a strong base.** This graph shows how the pH changes during the titration of 0.2000 *M* HCl with 0.2000 *M* NaOH.

Weak Acid–Strong Base Titrations

The calculations for the titration of a weak acid by a strong base are a bit more complex than when both the acid and base are strong. This is because we have to consider the equilibria involving the weak acid and its conjugate base. As an example, let's do the calculations and draw a titration curve for the titration of 25.0 mL of 0.2000 *M* $HC_2H_3O_2$ with 0.2000 *M* NaOH. The same four points are calculated but they use different equations.

The molecular and net ionic equations we will use are

$$HC_2H_3O_2 + NaOH \longrightarrow NaC_2H_3O_2 + H_2O$$

$$HC_2H_3O_2 + OH^- \longrightarrow C_2H_3O_2^- + H_2O$$

Because the concentrations of both solutions are the same, and because the acid and base react in a one-to-one mole ratio, we know that we will need exactly 25.0 mL of the base to reach the equivalence point. With this as background, let's look at what is involved in calculating the pH at various points along the titration curve.

■ The equivalence point in a titration can be found using a pH meter by plotting pH versus volume of base added and noting the sharp rise in pH. If a pH meter is used, we don't have to use an indicator.

At the start the solution is simply a solution of the weak acid, $HC_2H_3O_2$. We must use K_a to calculate the pH. We have seen that in many situations the assumptions hold and the calculations are summarized as

■ $[H^+] = \sqrt{K_a\ M_{HA}}$

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{(0.200 - x)} \approx \frac{(x)(x)}{(0.200)} = 1.8 \times 10^{-5}$$

$$x^2 = 3.6 \times 10^{-6} \text{ (rounded)}$$

$$x = [H^+] = 1.9 \times 10^{-3}$$

This result gives us a pH of 2.72. This is the pH before any NaOH is added.

Between the start and the equivalence point. As we add NaOH to the $HC_2H_3O_2$, the chemical reaction produces $C_2H_3O_2^-$, so the solution contains both $HC_2H_3O_2$ and $C_2H_3O_2^-$ (it is a buffer solution). Our equilibrium law can be rearranged to read

$$[H^+] = \frac{K_a[HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{K_a(\text{mol } HC_2H_3O_2)}{(\text{mol } C_2H_3O_2^-)}$$

Now all we need to do is solve a limiting reactant calculation to determine the moles of acetic acid, $HC_2H_3O_2$, left after each addition of NaOH and at the same time calculate the moles of acetate ion, $C_2H_3O_2^-$, formed.

Let's see what happens when we add 10.00 mL of NaOH solution. The initial moles of acetic acid are

■ Recall from Chapter 5 that molarity multiplied by volume (in liters) gives moles of solute.

$$0.2000\ M\ HC_2H_3O_2 \times 0.02500 \text{ L} = 5.000 \times 10^{-3} \text{ mol } HC_2H_3O_2$$

the moles of NaOH added are

$$0.20000\ M \text{ NaOH} \times 0.01000 \text{ L} = 2.000 \times 10^{-3} \text{ mol NaOH}$$

The moles of acetic acid left are

$$5.000 \times 10^{-3} \text{ mol} - 2.000 \times 10^{-3} \text{ mol} = 3.000 \times 10^{-3} \text{ mol } HC_2H_3O_2$$

From the chemical equations above, the moles of NaOH added are stoichiometrically equal to the moles of acetate ion formed. We therefore have 2.000×10^{-3} mol $C_2H_3O_2^-$. Entering the values for the K_a and the moles of acetic acid and acetate ions we get

$$[H^+] = \frac{(1.8 \times 10^{-5})(3.000 \times 10^{-3}\ \text{mol}\ HC_2H_3O_2)}{(2.000 \times 10^{-3}\ \text{mol}\ C_2H_3O_2^-)} = 2.7 \times 10^{-5}\ M$$

■ $[H^+] = K_a \dfrac{M_AV_A - M_BV_B}{M_BV_B}$

and the pH is 4.57. We can obtain more data points by selecting volumes of added NaOH between zero and 25 mL and repeating the calculation methods we just used. To generate a very large number of data points, repetitive calculations can be performed using a spreadsheet and the equations used above.

At the equivalence point. Here all the $HC_2H_3O_2$ has reacted and the solution contains the salt $NaC_2H_3O_2$ (i.e., we have a mixture of the ions Na^+ and $C_2H_3O_2^-$).

We began with 5.00×10^{-3} mol of $HC_2H_3O_2$, so we now have 5.00×10^{-3} mol of $C_2H_3O_2^-$ (in 0.0500 L). The concentration of $C_2H_3O_2^-$ is

$$[C_2H_3O_2^-] = \frac{5.00 \times 10^{-3}\ \text{mol}}{0.0500\ \text{L}} = 0.100\ M$$

Because $C_2H_3O_2^-$ is a base, we have to use K_b and write the chemical equation for the reaction of a base with water.

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

$$K_b = \frac{[OH^-][HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{K_w}{K_a} = 5.6 \times 10^{-10}$$

Substituting into the mass action expression gives

■ $[OH^-] = \sqrt{K_b \dfrac{M_AV_A}{V_A + V_B}}$

$$\frac{[OH^-][HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{(x)(x)}{0.100 - x} \approx \frac{(x)(x)}{0.100} = 5.6 \times 10^{-10}$$

$$x^2 = 5.6 \times 10^{-11}$$

$$x = [OH^-] = 7.5 \times 10^{-6}\ M$$

■ It is interesting that although we describe the overall reaction in the titration as *neutralization*, at the equivalence point the solution is slightly basic, not neutral.

The pOH calculates to be 5.12. Finally, the pH is (14.00 − 5.12) or 8.88. The pH at the equivalence point in this titration is 8.88, which is somewhat basic because the solution contains the Brønsted base, $C_2H_3O_2^-$. *In the titration of any weak acid with a strong base, the pH at the equivalence point will be greater than 7.*

After the equivalence point. Now the additional OH^- beyond the equivalence point shifts the following equilibrium to the left:

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

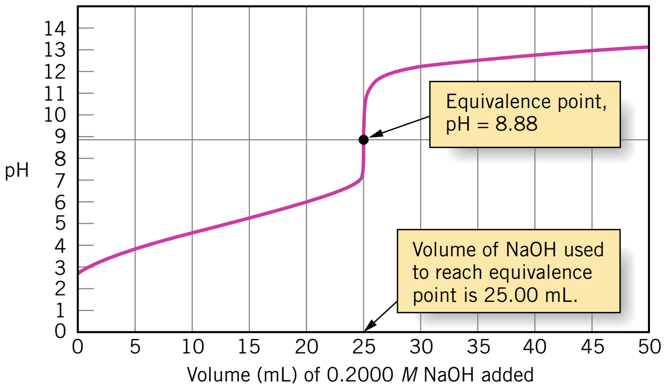
The production of OH^- *by this route* is thus suppressed as we add more and more NaOH solution. The only source of OH^- that affects the pH is from the base added after the equivalence point. From here on, therefore, the pH calculations become identical to those for the last half of the titration curve for HCl and NaOH shown above. Each point is just a matter of calculating the additional number of moles of NaOH, calculating the new final volume, taking their ratio (to obtain the molar concentration), and then calculating pOH and pH.

■ $[OH^-] = \dfrac{M_BV_B - M_AV_A}{V_A + V_B}$

Table 17.6 summarizes the titration data, and the titration curve is given in Figure 17.8. Once again, notice how the change in pH occurs slowly at first, then shoots up through the equivalence point, and finally looks just like the last half of the curve in Figure 17.7.

Table 17.6 **Titration of a Weak Acid with a Strong Base. The sample is 25.00 mL of 0.2000 *M* $HC_2H_3O_2$ and the titrant is 0.2000 *M* NaOH.**

Volume of Base Added (mL)	Molar Concentration of Species in Parentheses	pH
None	1.9×10^{-3} (H^+)	2.72
10.00	2.7×10^{-5} (H^+)	4.57
24.90	7.2×10^{-8} (H^+)	7.14
24.99	7.1×10^{-9} (H^+)	8.14
25.00	7.5×10^{-6} (OH^-)	8.88
25.01	4.0×10^{-5} (OH^-)	9.60
25.10	4.0×10^{-4} (OH^-)	10.60
26.00	3.9×10^{-3} (OH^-)	11.59
35.00	3.3×10^{-2} (OH^-)	12.52



Equivalence point, pH = 8.88

Volume of NaOH used to reach equivalence point is 25.00 mL.

Figure 17.8 | **Titration curve for titrating a weak acid with a strong base.** In this titration, we follow the pH as 0.2000 *M* acetic acid is titrated with 0.2000 *M* NaOH.

Practice Exercises

17.45 | When a weak acid such as acetic acid, $HC_2H_3O_2$, is titrated with KOH what are ALL of the species in solution at (a) the equivalence point, (b) at the start of the titration, (c) after the equivalence point and (d) before the equivalence point. For each part list the species in order from highest concentration to lowest. (*Hint:* H_2O should be the first item in all your lists and either [H^+] or [OH^-] should be the lowest.)

17.46 | Suppose we titrate 20.0 mL of 0.100 *M* $HCHO_2$ with 0.100 *M* NaOH. Calculate the pH (a) before any base is added, (b) when half of the $HCHO_2$ has been neutralized, (c) after a total of 15.0 mL of base has been added, and (d) at the equivalence point.

17.47 | Suppose 30.0 mL of 0.15 *M* NaOH is added to 50.0 mL of 0.20 *M* $HCHO_2$. What will be the pH of the resulting solution?

Weak Base–Strong Acid Titrations

The calculations involved here are nearly identical to those of the weak acid–strong base titration. We will review what is required but will not actually perform the calculations.

If we titrate 25.00 mL of 0.2000 *M* NH_3 with 0.2000 *M* HCl, the molecular and net ionic equations are

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$
$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

Before the titration begins. The solution at this point is simply a solution of the weak base, NH_3. Since the only solute is a base, we must use K_b to calculate the pH.

Between the start and the equivalence point. As we add HCl to the NH_3, the neutralization reaction produces NH_4^+, so the solution contains both NH_3 and NH_4^+ (it is a buffer solution). We do a limiting reactant calculation to determine the moles of ammonia left and the moles of ammonium ions produced by the addition of HCl. We use the equilibrium law to perform the calculation as we did with the weak acid.

At the equivalence point. Here all the NH_3 has reacted and the solution contains the salt NH_4Cl. We calculate the concentration of ammonium ions and then use the techniques we developed to determine the pH of the conjugate acid of a weak base.

After the equivalence point. The H^+ introduced by further addition of HCl has nothing with which to react, so it causes the solution to become more and more acidic. The concentration of H^+ calculated from the excess of HCl is used to calculate the pH.

Figure 17.9 illustrates the titration curve for this system.

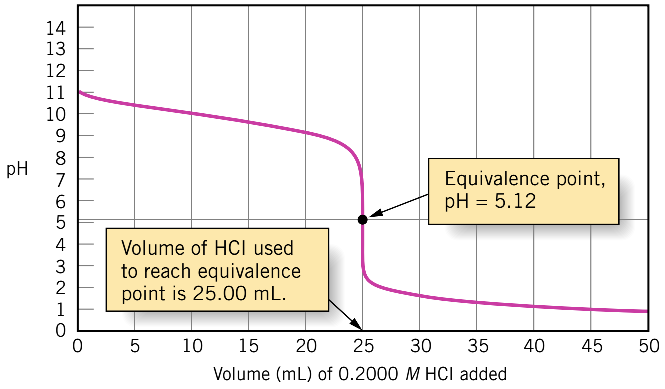


Figure 17.9 | **Titration curve for the titration of a weak base with a strong acid.** This graph shows how the pH changes as 0.2000 M NH_3 is titrated with 0.2000 M HCl.

Titration Curves for Diprotic Acids

When a weak diprotic acid such as ascorbic acid (vitamin C) is titrated with a strong base, there are two protons to be neutralized and there are two equivalence points. Provided that the values of K_{a_1} and K_{a_2} differ by at least four powers of 10, the neutralization takes place stepwise and the resulting titration curve shows two sharp increases in pH. We won't perform the calculations here because they're complex, but it is important to recognize the general shape of the titration curve, which is shown in Figure 17.10.

Acid–Base Indicators

■ Indicators and other molecules can absorb part of the visible spectrum of light. What is not absorbed is observed as the color. If a molecule absorbs the red and yellow wavelengths of light, it will look blue.

In Chapter 5 you learned that the end point of a titration could be detected when the color of the solution changed dramatically from one color to another. The substance that changed color was an acid–base indicator. Now we can understand how such indicators work.

Most dyes used as acid–base indicators are also weak acids. Therefore, let's represent an indicator molecule by the formula H*In*. In its un-ionized state, H*In* has one color. Its

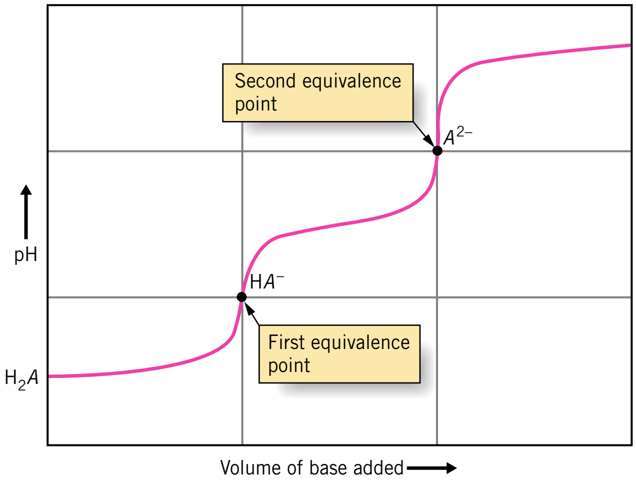


Figure 17.10 | **Titration of a diprotic acid, H_2A, by a strong base.** As each equivalence point is reached, there is a sharp rise in the pH.

Table 17.7 Common Acid—Base Indicators

Indicator	Approximate pH Range over which the Color Changes	Color Change (lower to higher pH)
Methyl green	0.2—1.8	Yellow to blue
Thymol blue	1.2—2.8	Yellow to blue
Methyl orange	3.2—4.4	Red to yellow
Ethyl red	4.0—5.8	Colorless to red
Methyl purple	4.8—5.4	Purple to green
Bromocresol purple	5.2—6.8	Yellow to purple
Bromothymol blue	6.0—7.6	Yellow to blue
Phenol red	6.4—8.2	Yellow to red/violet
Litmus	4.7—8.3	Red to blue
Cresol red	7.0—8.8	Yellow to red
Thymol blue	8.0—9.6	Yellow to blue
Phenolphthalein	8.2—10.0	Colorless to pink
Thymolphthalein	9.4—10.6	Colorless to blue
Alizarin yellow R	10.1—12.0	Yellow to red
Clayton yellow	12.2—13.2	Yellow to amber

conjugate base, In^-, has a different color, the more strikingly different the better. In solution, the indicator is involved in a typical acid–base equilibrium:

$$\underset{\substack{\text{Acid form}\\\text{(one color)}}}{\mathrm{H}In(aq)} \rightleftharpoons \mathrm{H}^+(aq) + \underset{\substack{\text{base form}\\\text{(another color)}}}{In^-(aq)}$$

How acid-base indicators work

The corresponding acid ionization constant, K_{In}, is given by

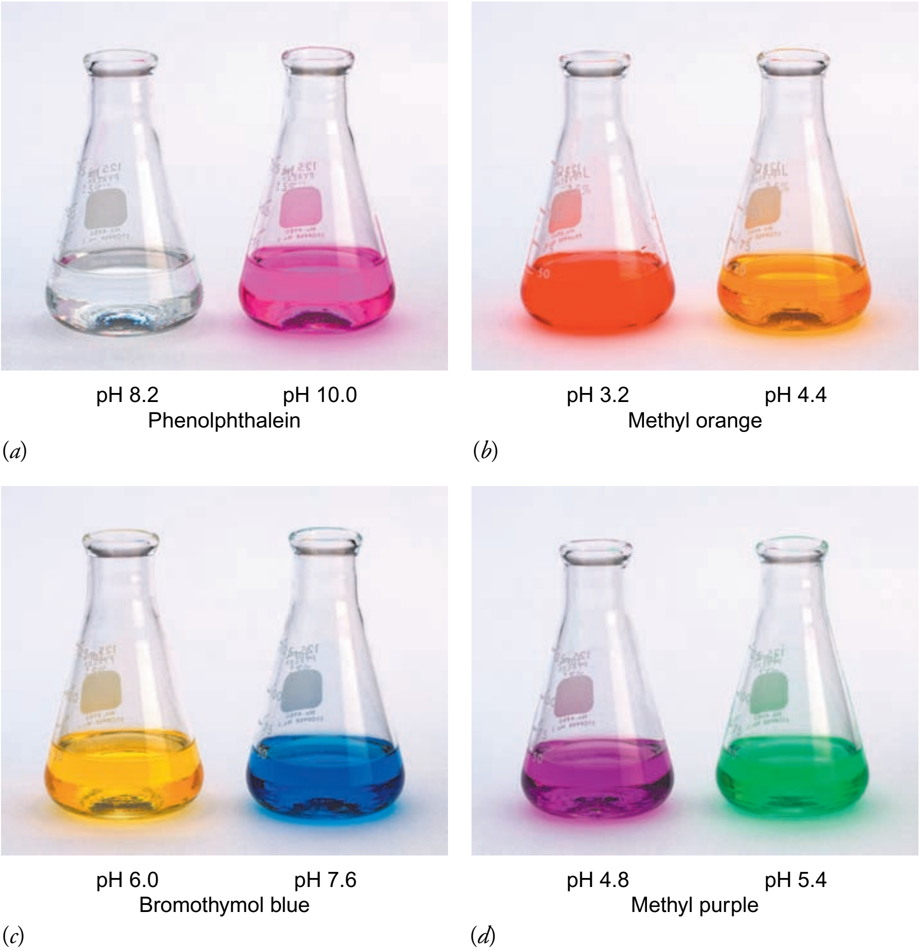
$$K_{\mathrm{In}} = \frac{[\mathrm{H}^+][In^-]}{[\mathrm{H}In]}$$

In a strongly acidic solution, when the H^+ concentration is high, the equilibrium is shifted to the left and most of the indicator molecules exist in its protonated or "acid form." Under these conditions, the color we observe is that of $\mathrm{H}In$. If the solution is made basic, the H^+ concentration decreases and the equilibrium shifts to the right, toward In^-, and the color we observe is that of the unprotonated "base form" of the indicator. Table 17.7 provides approximate pH ranges for the color changes of some common pH indicators.

It is generally agreed that if the ratio of $[\mathrm{HIn}]/[\mathrm{In}^-]$ is greater than 10 (i.e., the pH is 1 pH unit below the $\mathrm{p}K_{\mathrm{In}}$) the eye will see the color associated with the $\mathrm{H}In$ molecule. If the same ratio is less than 0.1 (i.e., the pH is 1 pH unit above the $\mathrm{p}K_{\mathrm{In}}$), the color seen is that of the anion In^-.

In typical acid–base titrations, we see that as we pass the equivalence point there is a sudden and large change in the pH, as shown in Figures 17.7–17.10. For example, in the titration of HCl with NaOH described earlier, the pH just one-half drop before the equivalence point (when 24.97 mL of the base has been added) is 3.92. Just one drop later (when 25.03 mL of base has been added) we have passed the equivalence point and the pH has risen to 10.08. This large swing in pH (from 3.92 to 10.08) causes a sudden shift in the position of equilibrium for the indicator, and we go from a condition where most

Figure 17.11 | **Colors of some common acid–base indicators.** *(Andy Washnik)*



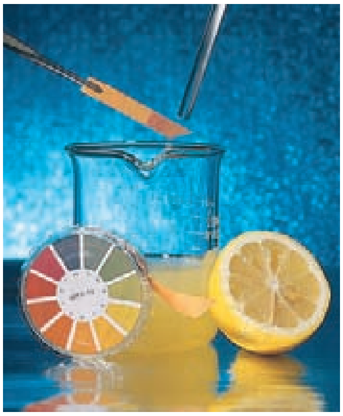


Figure 17.12 | **Using a pH test paper.** The color of this Hydrion test strip changed to orange when a drop of the lemon juice solution in the beaker was placed on it. According to the color code, the pH of the solution is closer to 3 than to the color for pH 5. *(Andy Washnik)*

■ Litmus is extracted from a type of moss called lichens.

of the indicator molecules are in the acid form to a condition in which most are in the base form. This is observed visually as a change in color from that of the acid form to that of the base form.

Measuring and Estimating pH

Earlier we saw that pH is usually measured with an instrument called a pH meter (Figure 17.2). We can now understand that a buffer solution is used to calibrate the pH meter because the pH of a buffer is reasonably stable. Typically, the accuracy of a pH meter is limited by the ±0.02 pH unit accuracy of the standardizing buffer. Modern pH meters can give much more precise readings if we are interested in changes in pH rather than the absolute pH value.

Another less precise method of obtaining the pH uses acid–base indicators. Table 17.7 gives several examples. Indicators change color over a narrow range of pH values, and Figure 17.11 shows the colors of some indicators at opposite ends of their color-change ranges. In addition, pH test papers are available that are impregnated with one or more indicator dyes. To obtain a rough idea of the pH, a drop of the solution to be tested is touched to a strip of the test paper and the resulting color is compared with a color code. Some commercial test papers (e.g., Hydrion) are impregnated with several dyes, with their containers carrying the color code (see Figure 17.12). Litmus paper was one of the first pH test papers ever made, and it is still commonly found in chemistry labs. It consists of porous paper impregnated with litmus dye, made either red or blue by exposure to acid or base and then dried.

Below pH 4.7 litmus is red, and above pH 8.3 it is blue. The transition for the color change occurs over a pH range of 4.7 to 8.3 with the center of the change at about 6.5, very nearly a neutral pH. To test whether a solution is acidic, a drop of it is placed on blue litmus paper. If the dye turns pink, the solution is acidic. Similarly, to test if the solution is basic, a drop is touched to red litmus paper. If the dye turns blue, the solution is basic. If a solution is close to neutral, neither red nor blue litmus will change color.

Summary

The Autoionization of Water and the pH Concept. Water reacts with itself to produce small amounts of H_3O^+ (often abbreviated H^+) and OH^- ions. The concentrations of these ions, both in pure water and dilute aqueous solutions, are related by the expression

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

$\boldsymbol{K_w}$ is the **ion product constant of water.** In pure water

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}$$

The **pH** of a solution is defined by the equation, pH $= -\log [H^+]$. Normally pH is measured with a pH meter and as the pH decreases, the acidity, or $[H^+]$, increases. The comparable term, **pOH** ($= -\log [OH^-]$), is used to describe a solution that is basic. As the hydroxide ion concentration decreases, the pOH increases. The pH and pOH are related by the expression

$$\text{pH} + \text{pOH} = 14.00$$

A solution is acidic if the hydrogen ion concentration exceeds 1.0×10^{-7} or the pH is less than 7.00. Similarly, a solution is basic if the hydroxide ion concentration exceeds 1.0×10^{-7} or if the pH is greater than 7.00.

Solutions of Strong Acids and Strong Bases. When calculating the pH of strong acids or strong bases, we assume that they are 100% ionized. The autoionization of water is suppressed in acid solutions and basic solutions. The result is that the hydrogen ion or hydroxide ion concentration from the autoionization of water is negligible.

Acid and Base Ionization Constants. A weak acid HA ionizes according to the general equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

or more simply,

$$HA \rightleftharpoons H^+ + A^-$$

The equilibrium constant is called the **acid ionization constant,** $\boldsymbol{K_a}$ (sometimes called an *acid dissociation constant*).

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

A weak base B ionizes by the general equation

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

The equilibrium constant is called the **base ionization constant,** $\boldsymbol{K_b}$ (sometimes called a *base dissociation constant*).

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The smaller the values of K_a (or K_b), the weaker are the substances as Brønsted acids (or bases).

Another way to compare the relative strengths of acids or bases is to use the negative logarithms of K_a and K_b, called **p$\boldsymbol{K_a}$** and **p$\boldsymbol{K_b}$,** respectively.

$$pK_a = -\log K_a \qquad pK_b = -\log K_b$$

Stronger acids or bases have *smaller* pK_a or pK_b values, respectively. For a conjugate acid–base pair,

$$K_a \times K_b = K_w$$

and

$$pK_a + pK_b = 14.00 \quad \text{(at 25 °C)}$$

Equilibrium Calculations—Determining K_a and K_b. The values of K_a and K_b can be obtained from initial concentrations of the acid or base and either the pH of the solution or the percentage ionization of the acid or base. The measured pH gives the equilibrium value for $[H^+]$. The **percentage ionization** is defined as

$$\text{percentage ionization} = \frac{\text{amount ionized}}{\text{amount available}} \times 100\%$$

Equilibrium Calculations—Determining Equilibrium Concentrations When K_a or K_b Is Known. Problems fall into one of three categories: (1) the only solute is a weak acid (we must use the K_a expression), (2) the only solute is a weak base (we must use the K_b expression), and (3) the solution contains both a weak acid and its conjugate base (we can use either K_a or K_b).

When the initial concentration of the acid (or base) is larger than 100 times the value of K_a (or K_b), it is safe to use initial concentrations of acid or base as though they were equilibrium values in the mass action expression. When this approximation cannot be used, we can use the quadratic formula.

Ions as Acids or Bases. A solution of a salt is acidic if the cation is acidic but the anion is neutral. Metal ions with high charge densities generally are acidic, but those of Groups 1A and 2A (except Be^{2+}) are not. Cations such as NH_4^+, which are the conjugate acids of weak *molecular* bases, are themselves proton donors and are acidic.

When the anion of a salt is the conjugate base of a *weak* acid, the anion is a weak base. Anions of strong acids, such as Cl^- and NO_3^-, are such weak Brønsted bases that they cannot affect the pH of a solution.

If the salt is derived from a weak acid *and* a weak base, its net effect on pH has to be determined on a case-by-case basis by determining which of the two ions is the stronger.

Buffers.

A solution that contains both a weak acid and a weak base (usually an acid–base conjugate pair) is called a **buffer,** because it is able to absorb $[H^+]$ from a strong acid or $[OH^-]$ from a strong base without large changes in pH. For the general acid–base pair, HA and A^-, the following reactions neutralize H^+ and OH^-. When H^+ is added to the buffer:

$$A^- + H^+ \longrightarrow HA$$

When OH^- is added to the buffer:

$$HA + OH^- \longrightarrow A^- + H_2O$$

The pH of a buffer is controlled by the ratio of weak acid to weak base, expressed either in terms of molarities or moles.

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \times \frac{\text{moles } HA}{\text{moles } A^-}$$

Because the $[H^+]$ is determined by the mole ratio of HA to A^-, dilution does not change the pH of a buffer. The **Henderson–Hasselbalch equation,**

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

can be used to calculate the pH directly from the $\text{p}K_a$ of the acid and the concentrations of the conjugate acid, HA, and base, A^-.

In performing buffer calculations, the usually valid simplifications are

$$[HA]_{\text{equilibrium}} \approx [HA]_{\text{initial}}$$
$$[A^-]_{\text{equilibrium}} \approx [A^-]_{\text{initial}}$$

The value of $[A^-]_{\text{initial}}$ is found from the molarity of the *salt* of the weak acid in the buffer. Once $[H^+]$ is found by this calculation, the pH is calculated.

Buffer calculations can also be performed using K_b for the weak base component. Similar equations apply, the principal difference being that it is the OH^- concentration that is calculated. Thus, using K_b we have

$$[OH^-] = K_b \times \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$
$$= K_b \times \frac{(\text{moles conjugate base})}{(\text{moles conjugate acid})}$$

Buffers are most effective when the $\text{p}K_a$ of the acid member of the buffer pair lies within ± 1 unit of the desired pH.

Equilibria in Solutions of Polyprotic Acids.

A polyprotic acid has a K_a value for the ionization of each of its hydrogen ions. Successive values of K_a often differ by a factor of 10^4 to 10^5. This allows us to calculate the pH of a solution of a polyprotic acid by using just the value of K_{a_1}. If the polyprotic acid is the only solute, the anion formed in the second step of the ionization, A^{2-}, has a concentration equal to K_{a_2}.

The anions of weak polyprotic acids are bases that react with water in successive steps, the last of which has the molecular polyprotic acid as a product. For a diprotic acid, $K_{b_1} = K_w/K_{a_2}$ and $K_{b_2} = K_w/K_{a_1}$. Usually, $K_{b_1} \gg K_{b_2}$, so virtually all the OH^- produced in the solution comes from the first step. The pH of the solution can be calculated using just K_{b_1} and the reaction

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^-.$$

Acid–Base Titrations and Indicators.

Neutralization titrations can be experimentally measured using a pH meter or they can be calculated using the principles developed in this chapter. Both methods yield the same result, a titration curve. The titration curve contains important information about the chemical system including the equivalence point and equilibrium constant data.

Each calculated titration curve has four distinct calculations:

(a) The starting pH of a solution that contains only an acid or base
(b) The pH values for titrant volumes between the start and the equivalence points
(c) The pH at the equivalence point
(d) The pH values for titrant volumes past the equivalence point

A graph of the pH values versus the volume of titrant gives us a titration curve. Titration curves show a sharp change in pH at the equivalence point. **Titration curves** also have distinct differences in shape when strong acid–strong base titrations are compared to weak acid–weak base titrations.

Acid–base indicators are weak acids in which the conjugate acid and base have different colors. The sudden change in pH at the equivalence point causes a rapid shift from one color of the indicator to the other. If matched to the equivalence point, a pH indicator will change color abruptly when a titration reaches the equivalence point.

Tools for Problem Solving The concepts that you've learned in this chapter can be applied as tools in solving problems. If necessary, refer to this table when working on the review exercises and problems that follow.

Ion product constant of water, K_w (page 774)

$$K_w = [H^+][OH^-] \qquad \text{or} \qquad K_w = [H_3O^+][OH^-]$$

At 25 °C the value of K_w is 1.0×10^{-14}. This equation allows us to convert between hydrogen (hydronium) ion concentrations and hydroxide ion concentrations. It also demonstrates that the hydrogen ion concentration is inversely proportional to the hydroxide concentration.

Definition of pH (page 776)

$$\text{pH} = -\log [H^+]$$

The pH scale was developed to conveniently represent the very small numbers usually encountered when working with acid–base equilibria. As the hydrogen ion concentration increases, the pH decreases.

Defining the p-function, pX (page 777)

$$\text{p}X = -\log X$$

A p-function is formulated as the logarithm of a value with the sign changed. As with pH, it is a convenient way to represent very small numbers.

Relating pH and pOH to pK_w (page 777)

$$\text{pH} + \text{pOH} = \text{p}K_w$$

Adding the pH and pOH always gives us 14.00 at 25 °C. This is an easy way to convert between pH and pOH.

General equation for the ionization of a weak acid (page 780)

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad \text{or} \qquad HA \rightleftharpoons H^+ + A^-$$

You follow the form of the general equation to write the correct chemical equilibrium for a given weak acid, from which you construct the correct K_a expression.

General equation for the ionization of a weak base (page 782)

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

You follow the form of the general equation to write the correct chemical equilibrium for a given weak base, from which you construct the correct K_b expression.

Inverse relationship between K_a and K_b (page 783)

$$K_a \times K_b = K_w$$

Use this equation to calculate K_a, given K_b, or vice versa.

Relationship between pK_a and pK_b (page 783)

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

This equation allows us to determine the equilibrium constant of a conjugate base if we know the equilibrium constant of the conjugate acid and vice versa.

Percentage ionization (page 784)

$$\text{percentage ionization} = \frac{\text{moles per liter ionized}}{\text{moles per liter available}} \times 100\%$$

Use this equation to calculate the percentage ionization from the initial concentration of acid (or base) and the change in the concentrations of the ions. If the percentage ionization is known, you can calculate the change in the concentration of the acid or base and then use that information to calculate the K_a (or K_b).

Criterion for predicting if simplifying assumptions will work (page 793)

$$C_{HA} > 100 \times K_a \qquad \text{or} \qquad C_B > 100 \times K_b$$

If this relationship is true, initial concentrations can be used as though they are equilibrium values in the mass action expression when working acid–base equilibrium problems. The error from this assumption is a maximum of 5% in $[H^+]$ or $[OH^-]$. If the condition fails, then we have to use the quadratic equation or the method of successive approximations.

Identification of acidic cations and basic anions (pages 794 and 795)

We use the concepts developed here to determine whether a salt solution is acidic, basic, or neutral. This is also the first step in calculating the pH of a salt solution.

How buffers work (page 798)

These reactions illustrate how the concentrations of conjugate acid and base change when a strong acid or strong base is added to a buffer. Adding H^+ decreases $[A^-]$ and increases $[HA]$; adding OH^- decreases $[HA]$ and increases $[A^-]$. These reactions keep the pH of the solution from changing drastically.

Polyprotic acids ionize stepwise (page 805)

Polyprotic acids have more than one ionizable proton in their formulas. Each proton will ionize sequentially and the chemical equation will have a form similar to the general equation for the ionization of a weak acid tool above.

Titration curves have four regions (pages 811 to 815)

A titration curve is a graph of the pH as a function of the volume of titrant added to a sample. To plot such a curve, there are four different stages of calculation. They are (a) the starting point, (b) the stage from the start to the equivalence point, (c) the equivalence point, and (d) the stage after the equivalence point.

How acid-base indicators work (page 817)

Titration indicators are weak acids that have one color for the conjugate acid and a different color for the conjugate base. Whether the indicator is in the conjugate acid or conjugate base form depends on the pH. The rapid, large change in pH at a titration end point results in a distinct color change that signals a titration end point.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Ionization of Water and the pH Concept

17.1 Write the chemical equation for **(a)** the autoionization of water and **(b)** the equilibrium law for K_w.

17.2 How are acidic, basic, and neutral solutions in water defined **(a)** in terms of $[H^+]$ and $[OH^-]$ and **(b)** in terms of pH and pOH?

17.3 At 25 °C, how are the pH and pOH of a solution related to each other?

17.4 Explain how acids and bases suppress the ionization of water, often called the common ion effect.

17.5 Explain the leveling effect of water.

Strong Acids and Strong Bases

17.6 List the strong acids.

17.7 What chemical property is central to our classifying an acid as a strong acid?

17.8 How are strong bases identified?

17.9 Some strong bases can be used to safely reduce stomach acidity (heartburn). What differentiates strong bases that are safe medicines from those that could cause irreparable harm?

Acid and Base Ionization Constants: K_a, K_b, pK_a, and pK_b

17.10 Write the general equation for the ionization of a weak acid, H*A*, in water. Give the equilibrium law corresponding to K_a.

17.11 Write the chemical equation for the ionization of each of the following weak acids in water. (For polyprotic acids, write only the equation for the first step in the ionization.)

(a) HNO_2 **(c)** $HAsO_4^{2-}$

(b) H_3PO_4 **(d)** $(CH_3)_3NH^+$

17.12 For each of the acids in Review Question 17.11 write the appropriate K_a expression.

17.13 Write the general equation for the ionization of a weak base, *B*, in water. Give the equilibrium law corresponding to K_b.

17.14 Write the chemical equation for the ionization of each of the following weak bases in water.

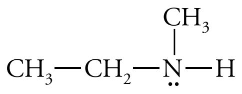
(a) $(CH_3)_3N$ **(c)** NO_2^-

(b) AsO_4^{3-} **(d)** $(CH_3)_2N_2H_2$

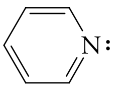
17.15 For each of the bases in Review Question 17.14, write the appropriate K_b expression.

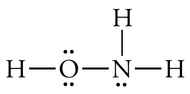
17.16 The pK_a of HCN is 9.31 and that of HF is 3.46. Which is the stronger Brønsted base, CN^- or F^-?

17.17 Write the structural formulas for the conjugate acids of the following:

(a) 

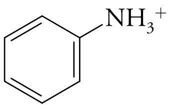
$CH_3{-}CH_2{-}\overset{\begin{array}{c}CH_3\\|\end{array}}{\underset{\cdot\cdot}{N}}{-}H$

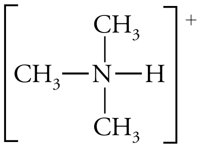
(b) 

(c) 

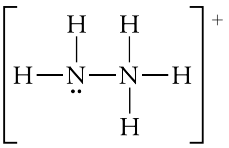
$H{-}\ddot{\underset{\cdot\cdot}{O}}{-}\overset{\begin{array}{c}H\\|\end{array}}{\underset{\cdot\cdot}{N}}{-}H$

17.18 Write the structural formulas for the conjugate bases of the following:

(a) 

(b) 

$\left[CH_3{-}\overset{\begin{array}{c}CH_3\\|\end{array}}{\underset{\begin{array}{c}|\\CH_3\end{array}}{N}}{-}H\right]^+$

(c) 

$\left[H{-}\overset{\begin{array}{c}H\\|\end{array}}{\underset{\cdot\cdot}{N}}{-}\overset{\begin{array}{c}H\\|\end{array}}{\underset{\begin{array}{c}|\\H\end{array}}{N}}{-}H\right]^+$

17.19 How is percentage ionization defined? Write the equation.

17.20 What criterion do we use to determine whether or not the equilibrium concentration of an acid or base will be effectively the same as its initial concentration when we calculate the pH of the solution?

17.21 For which of the following are we permitted to make the assumption that the equilibrium concentration of the acid or base is the same as the initial concentration when we calculate the pH of the solution specified?

(a) 0.020 *M* $HC_2H_3O_2$ **(c)** 0.002 *M* N_2H_4

(b) 0.10 *M* CH_3NH_2 **(d)** 0.050 *M* $HCHO_2$

Acid–Base Properties of Salt Solutions

17.22 Aspirin is acetylsalicylic acid, a monoprotic acid whose K_a value is 3.3×10^{-4}. Does a solution of the sodium salt of aspirin in water test acidic, basic, or neutral? Explain.

17.23 The K_b value of the oxalate ion, $C_2O_4^{2-}$, is 1.6×10^{-10}. Is a solution of $K_2C_2O_4$ acidic, basic, or neutral? Explain.

17.24 Consider the following compounds and suppose that 0.5 *M* solutions are prepared of each: NaI, NH_4Br, KF, KCN, $KC_2H_3O_2$, $CsNO_3$, and Kbr. Write the *formulas* of those that have solutions that are **(a)** acidic, **(b)** basic, and **(c)** neutral.

17.25 Will an aqueous solution of $AlCl_3$ turn litmus red or blue? Explain.

17.26 A solution of hydrazinium acetate is slightly acidic. Without looking at the tables of equilibrium constants, is K_a for acetic acid larger or smaller than K_b for hydrazine? Justify your answer.

***17.27** When ammonium nitrate is added to a suspension of magnesium hydroxide in water, the $Mg(OH)_2$ dissolves. Write a net ionic equation to show how this occurs.

Buffers

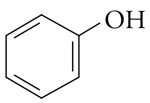
17.28 Write ionic equations that illustrate how each pair of compounds can serve as a buffer pair.

(a) H_2CO_3 and $NaHCO_3$ (the "carbonate" buffer in blood)

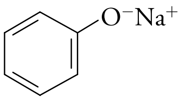
(b) NaH_2PO_4 and Na_2HPO_4 (the "phosphate" buffer inside body cells)

(c) NH_4Cl and NH_3

(d) Phenol and sodium phenolate



and



17.29 The hydrogen phosphate ion is able to act as a buffer all by itself. Write chemical equations that show how this ion reacts with **(a)** H^+ and **(b)** OH^-.

Ionization of Polyprotic Acids

17.30 When sulfur dioxide, an air pollutant from the burning of sulfur-containing coal or oil, dissolves in water, an acidic solution is formed that can be viewed as containing sulfurous acid, H_2SO_3.

$$H_2O + SO_2(g) \rightleftharpoons H_2SO_3(aq)$$

Write the expression for K_{a_1} and K_{a_2} for sulfurous acid.

17.31 Citric acid, found in citrus fruits, is a triprotic acid, $H_3C_6H_5O_7$. Write chemical equations for the three-step ionization of this acid in water and write the three K_a expressions (equilibrium laws).

17.32 What simplifying assumptions do we usually make in working problems involving the ionization of polyprotic acids? Why are they usually valid? Under what conditions do they fail?

Salts of Polyprotic Acids

17.33 Write the equations for the chemical equilibria that exist in solutions of **(a)** Na_2SO_3, **(b)** Na_3PO_4, and **(c)** $K_2C_4H_4O_6$.

17.34 What simplifying assumptions do we usually make in working problems involving equilibria of salts of polyprotic acids? Why are they usually valid? Under what conditions do they fail?

Titrations and Acid–Base Indicators

17.35 Define the terms equivalence point and end point as they apply to an acid–base titration.

17.36 When a formic acid solution is titrated with sodium hydroxide, will the solution be acidic, neutral, or basic at the equivalence point?

17.37 When a solution of hydrazine is titrated with hydrochloric acid, will the solution be acidic, neutral, or basic at the equivalence point?

17.38 Qualitatively, describe how an acid–base indicator works. Why do we want to use a minimum amount of indicator in a titration?

17.39 If you use methyl orange in the titration of $HC_2H_3O_2$ with NaOH, will the end point of the titration correspond to the equivalence point? If not, suggest a better indicator for this titration. Justify your answer.

Review Problems

Autoionization of Water and pH

17.40 Deuterium oxide, D_2O, ionizes like water. At 20 °C its K_w or ion product constant, analogous to that of water, is 8.9×10^{-16}. Calculate $[D^+]$ and $[OD^-]$ in deuterium oxide at 20 °C. Calculate also the pD and the pOD.

17.41 At the temperature of the human body, 37 °C, the value of K_w is 2.5×10^{-14}. Calculate $[H^+]$, $[OH^-]$, pH, and pOH of pure water at this temperature. What is the relationship between pH, pOH, and pK_w at this temperature? Is water neutral at this temperature?

17.42 Calculate the $[H^+]$, pH, and pOH in each of the following solutions in which the hydroxide ion concentrations are

(a) $0.0068\ M$ **(c)** $1.6 \times 10^{-8}\ M$

(b) $6.4 \times 10^{-5}\ M$ **(d)** $8.2 \times 10^{-12}\ M$

17.43 Calculate the $[OH^-]$, pH, and pOH for each of the following solutions in which the H^+ concentrations are

(a) $3.5 \times 10^{-7}\ M$ **(c)** $2.5 \times 10^{-11}\ M$

(b) $0.0017\ M$ **(d)** $7.9 \times 10^{-2}\ M$

17.44 A certain brand of beer had a H^+ concentration equal to 1.9×10^{-5} mol L^{-1}. What is the pH of the beer?

17.45 A soft drink was put on the market with $[H^+] = 1.4 \times 10^{-5}$ mol L^{-1}. What is its pH?

17.46 Calculate the molar concentrations of H^+ and OH^- in solutions that have the following pH values.

(a) 8.14 **(b)** 2.56 **(c)** 11.25 **(d)** 13.28 **(e)** 6.70

17.47 Calculate the molar concentrations of H^+ and OH^- in solutions that have the following pOH values.

(a) 12.27 **(b)** 6.14 **(c)** 10.65 **(d)** 4.28 **(e)** 3.76

17.48 The interaction of water droplets in rain with carbon dioxide that is naturally present in the atmosphere causes rain water to be slightly acidic because CO_2 is an acidic anhydride. As a result, pure clean rain has a pH of about 5.7. What are the hydrogen ion and hydroxide ion concentrations in this rain water?

17.49 "Acid rain" forms when rain falls through air polluted by oxides of sulfur and nitrogen, which dissolve to form acids such as H_2SO_3, H_2SO_4, and HNO_3. Trees and plants are affected if the acid rain has a pH of 3.5 or lower. What is the hydrogen ion concentration in acid rain that has a pH of 3.16? What is the pH of a solution having twice your calculated hydrogen ion concentration?

Solutions of Strong Acids and Bases

17.50 What is the concentration of H^+ in $0.00065\ M\ HNO_3$? What is the pH of this solution? What is the OH^- concentration in this solution?

17.51 What is the concentration of H^+ in $0.031\ M\ HClO_4$? What is the pH of the solution? What is the OH^- concentration in the solution? By how much does the pH change if the concentration of H^+ is doubled?

17.52 A sodium hydroxide solution is prepared by dissolving 6.0 g NaOH in 1.00 L of solution. What is the molar concentration of OH^- in the solution? What are the pOH and the pH of the solution? What is the hydrogen ion concentration in the solution?

17.53 A solution was made by dissolving 0.837 g $Ba(OH)_2$ in 100 mL final volume. What is the molar concentration of OH^- in the solution? What are the pOH and the pH? What is the hydrogen ion concentration in the solution?

17.54 A solution of $Ca(OH)_2$ has a measured pH of 11.60. What is the molar concentration of the $Ca(OH)_2$ in the solution? What is the molar concentration of $Ca(OH)_2$ if the solution is diluted so that the pH is 10.60?

17.55 A solution of HCl has a pH of 2.50. How many grams of HCl are there in 0.250 L of this solution? How many grams of HCl are in 250 mL of an HCl solution that has twice this pH?

17.56 In a 0.0020 *M* solution of NaOH, how many moles per liter of OH^- come from the ionization of water?

17.57 In a certain solution of HCl, the ionization of water contributes 3.4×10^{-11} moles per liter to the H^+ concentration. What is the total H^+ concentration in the solution?

***17.58** A solution was prepared with 2.64 micrograms of $Ba(OH)_2$ in 1.00 liter of water. What is the pH of the solution, and what concentration of hydrogen ions is provided by the ionization of water?

***17.59** What is the pH of a 3.0×10^{-7} *M* solution of HCl? What concentration of hydrogen ions is provided by the ionization of water?

***17.60** A 1.0 *M* solution of acetic acid has a pH of 2.37. What percentage of the acetic acid is ionized in the solution?

***17.61** A 0.250 *M* solution of NH_3 has a pH of 11.32. What percentage of the ammonia is ionized in this solution?

Acid and Base Ionization Constants: K_a, K_b, pK_a, and pK_b

17.62 The K_a for HF is 6.8×10^{-4}. What is the K_b for F^-?

17.63 The barbiturate ion, $C_4H_3N_2O_3^-$, has $K_b = 1.0 \times 10^{-10}$. What is the K_a for barbituric acid?

17.64 Lactic acid, $HC_3H_5O_3$, is responsible for the sour taste of old milk. At 25 °C, its $K_a = 1.4 \times 10^{-4}$. **(a)** What is the K_b of its conjugate base, the lactate ion, $C_3H_5O_3^-$? **(b)** Is its conjugate base a stronger or a weaker base than the acetate ion?

OH **17.65** Iodic acid, HIO_3, has a pK_a of 0.77. **(a)** What are the formula and the K_b of its conjugate base? **(b)** Is its conjugate base a stronger or a weaker base than the acetate ion?

Equilibrium Calculations

17.66 A 0.20 *M* solution of a weak acid, H*A*, has a pH of 3.22. What is the percentage ionization of the acid? What is the value of K_a for the acid?

17.67 If a weak base is 0.030% ionized in 0.030 *M* solution, what is the pH of the solution? What is the value of K_b for the base?

OH **17.68** Periodic acid, HIO_4, is an important oxidizing agent and a moderately strong acid. In a 0.10 *M* solution, $[H^+] = 3.8 \times 10^{-2}$ mol L^{-1}. Calculate the K_a and pK_a for periodic acid.

17.69 Chloroacetic acid, $HC_2H_2O_2Cl$, is a stronger monoprotic acid than acetic acid. In a 0.10 *M* solution, the pH is 1.96. Calculate the K_a and pK_a for chloroacetic acid.

ILW **17.70** Ethylamine, $CH_3CH_2NH_2$, has a strong, pungent odor similar to that of ammonia. Like ammonia, it is a Brønsted base. A 0.10 *M* solution has a pH of 11.87. Calculate the K_b and pK_b for ethylamine. What is the percentage ionization of ethylamine in this solution?

17.71 Hydroxylamine, $HONH_2$, like ammonia, is a Brønsted base. A 0.15 *M* solution has a pH of 10.11. What are the K_b and pK_b values for hydroxylamine? What is the percentage ionization of the $HONH_2$?

ILW ***17.72** What are the concentrations of all the solute species in 0.150 *M* lactic acid, $HC_3H_5O_2$? What is the pH of the solution? This acid has a $K_a = 1.4 \times 10^{-4}$.

***17.73** What are the concentrations of all the solute species in a 1.0 *M* solution of hydrogen peroxide, H_2O_2? What is the pH of the solution? For H_2O_2, $K_a = 2.4 \times 10^{-12}$.

17.74 Codeine, a cough suppressant extracted from crude opium, is a weak base with a pK_b of 5.80. What will be the pH of a 0.020 *M* solution of codeine? (Use *Cod* as a symbol for codeine.)

17.75 Pyridine, C_5H_5N, is a bad-smelling liquid that is a weak base in water. Its pK_b is 8.77. What is the pH of a 0.20 *M* aqueous solution of this compound?

17.76 A solution of acetic acid has a pH of 2.54. What is the concentration of acetic acid in this solution?

17.77 How many moles of NH_3 must be dissolved in water to give 500. 0 mL of solution with a pH of 11.22?

Equilibrium Calculations when Simplifications Fail

***17.78** What is the pH of a 0.0050 *M* solution of sodium cyanide?

***17.79** What is the pH of a 0.020 *M* solution of chloroacetic acid, for which $K_a = 1.4 \times 10^{-3}$?

17.80 The compound *para*-aminobenzoic acid (PABA) is a powerful sun-screening agent whose salts were once used widely in sun tanning and screening lotions. The parent acid, which we may symbolize as H-*Paba*, is a weak acid with a pK_a of 4.92 (at 25 °C). What are the $[H^+]$ and pH of a 0.030 *M* solution of this acid?

17.81 Barbituric acid, $HC_4H_3N_2O_3$ (which we will abbreviate H-*Bar*), was discovered by the Nobel Prize–winning organic chemist Adolph von Bayer and named after his friend, Barbara. It is the parent compound of widely used sleeping drugs, the barbiturates. Its pK_a is 4.01. What are the $[H^+]$ and pH of a 0.020 *M* solution of H-*Bar*?

Acid–Base Properties of Salt Solutions

17.82 Calculate the pH of 0.20 *M* NaCN. What is the concentration of HCN in the solution?

17.83 Calculate the pH of 0.40 *M* KNO_2. What is the concentration of HNO_2 in the solution?

ILW **17.84** Calculate the pH of 0.15 *M* CH_3NH_3Cl. For methylamine, CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

17.85 Calculate the pH of 0.10 *M* hydrazinium chloride, N_2H_5Cl.

17.86 A 0.18 *M* solution of the sodium salt of nicotinic acid (also known pharmaceutically as niacin) has a pH of 9.05. What is the value of K_a for nicotinic acid?

17.87 A weak base *B* forms the salt *B*HCl, composed of the ions BH^+ and Cl^-. A 0.15 *M* solution of the salt has a pH of 4.28. What is the value of K_b for the base *B*?

OH ***17.88** Liquid chlorine bleach is really nothing more than a solution of sodium hypochlorite, NaOCl, in water. Usually, the concentration is approximately 5.1% NaOCl by weight. Use this information to calculate the approximate pH of a bleach solution, assuming no other solutes are in the solution except NaOCl. (Assume the bleach has a density of 1.0 g/mL.)

***17.89** The conjugate acid of a molecular base has the general formula, BH^+ and a pK_a of 5.00. A solution of a salt of this cation, *BHY*, tests slightly basic. Will the conjugate acid of Y^-, H*Y*, have a pK_a greater than 5.00 or less than 5.00? Explain.

Buffers

17.90 What is the pH of a solution that contains 0.15 *M* $HC_2H_3O_2$ and 0.25 *M* $C_2H_3O_2^-$? Use $K_a = 1.8 \times 10^{-5}$ for $HC_2H_3O_2$.

17.91 Rework the preceding problem using the K_b for the acetate ion. (Be sure to write the proper chemical equation and equilibrium law.)

OH **17.92** A buffer is prepared containing 0.25 *M* NH_3 and 0.45 *M* NH_4^+. Calculate the pH of the buffer using the K_b for NH_3.

17.93 Calculate the pH of the buffer in the preceding problem using the K_a for NH_4^+.

***17.94** Certain proteolytic enzymes react in alkaline solutions. One of these enzymes produces 1.8 micromoles of hydrogen ions per second in a 2.50 mL portion of a buffer composed of 0.25 *M* NH_3 and 0.20 *M* NH_4Cl. By how much will the concentrations of the NH_3 and NH_4^+ ions change after the reaction has run for 35 seconds?

***17.95** A hydrolytic enzyme consumes 1.8×10^{-7} moles of hydrogen ions per minute in 2.50 mL of a buffer that contained 0.15 *M* $HC_2H_3O_2$ and 0.25 *M* $C_2H_3O_2^-$. By how much did the concentrations of $HC_2H_3O_2$ and $C_2H_3O_2^-$ change after the enzyme reacted for 3.45 minutes?

***17.96** By how much will the pH change if 0.025 mol of HCl is added to 1.00 L of the buffer in Review Problem 17.90?

***17.97** By how much will the pH change if 25.0 mL of 0.20 *M* NaOH is added to 0.500 L of the buffer in Review Problem 17.92?

***17.98** What are the initial and final pH values for the buffer in Review Problem 17.94? What is the change in pH?

***17.99** What are the initial and final pH values for the buffer in Review Problem 17.95? What is the change in pH?

17.100 How many grams of sodium acetate, $NaC_2H_3O_2$, would have to be added to 1.0 L of 0.15 *M* acetic acid (pK_a 4.74) to make the solution a buffer for pH 4.00?

17.101 How many grams of sodium formate, $NaCHO_2$, would have to be dissolved in 1.0 L of 0.12 *M* formic acid (pK_a 3.74) to make the solution a buffer for pH 3.50?

***17.102** Suppose 30.00 mL of 0.100 *M* HCl is added to an acetate buffer prepared by dissolving 0.100 mol of acetic acid and 0.110 mol of sodium acetate in 0.100 L of solution. What are the initial and final pH values? What would be the pH if the same amount of HCl solution were added to 125 mL of pure water?

***17.103** How many milliliters of 0.15 *M* HCl would have to be added to the original 0.100 L of the buffer described in Review Problem 17.92 to make the pH decrease by 0.05 pH unit? How many milliliters of the same HCl solution would, if added to 0.100 L of pure water, make the pH decrease by 0.05 pH unit?

Solutions of Polyprotic Acids

ILW ***17.104** Calculate the concentrations of all the solute species in a 0.15 *M* solution of ascorbic acid (vitamin C). What is the pH of the solution?

***17.105** Tellurium, in the same family as sulfur, forms an acid analogous to sulfuric acid and called telluric acid. It exists, however, as H_6TeO_6 (which can be understood as the formula $H_2TeO_4 + 2H_2O$). It is a diprotic acid with $K_{a_1} = 2 \times 10^{-8}$ and $K_{a_2} = 1 \times 10^{-11}$. Calculate the concentrations of H^+, $H_5TeO_6^-$, and $H_4TeO_6^{2-}$ in a 0.25 *M* solution of H_6TeO_6. What is the pH of the solution?

OH ***17.106** Calculate the concentrations of all of the solute species involved in the equilibria in a 2.0 *M* solution of H_3PO_4. Calculate the pH of the solution.

***17.107** What is the pH of a 0.25 *M* solution of arsenic acid, H_3AsO_4? In this solution, what are the concentrations of $H_2AsO_4^-$ and $HAsO_4^{2-}$?

***17.108** Phosphorous acid, H_3PO_3, is actually a diprotic acid for which $K_{a_1} = 5.0 \times 10^{-2}$ and $K_{a_2} = 2.0 \times 10^{-7}$. What are the values of $[H^+]$, $[H_2PO_3^-]$, and $[HPO_3^{2-}]$ in a 1.0 *M* solution of H_3PO_3? What is the pH of the solution?

17.109 What is the pH of a 0.20 *M* solution of oxalic acid, $H_2C_2O_4$?

Solutions of Salts of Polyprotic Acids

***17.110** Calculate the pH of 0.24 *M* Na_2SO_3. What are the concentrations of all ions and H_2SO_3 in the solution?

17.111 Calculate the pH of 0.33 *M* K_2CO_3. What are the concentrations of all ions and H_2CO_3 in the solution?

OH **17.112** Sodium citrate, $Na_3C_6H_5O_7$, is used as an anticoagulant in the collection of blood. What is the pH of a 0.10 *M* solution of this salt?

17.113 What is the pH of a 0.25 *M* solution of sodium oxalate, $Na_2C_2O_4$?

***17.114** What is the pH of a 0.50 *M* solution of Na_3PO_4? In this solution, what are the concentrations of HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4?

17.115 The pH of a 0.10 *M* Na_2CO_3 solution is adjusted to 12.00 using a strong base. What is the concentration of HCO_3^- in this solution?

Acid–Base Titrations

17.116 When 50.0 mL of 0.050 *M* formic acid, $HCHO_2$, is titrated with 0.050 *M* sodium hydroxide, what is the pH at the equivalence point? (Be sure to take into account the change in volume during the titration.) Select a good indicator for this titration from Table 17.7.

17.117 When 25 mL of 0.12 *M* aqueous ammonia is titrated with 0.12 *M* hydrobromic acid, what is the pH at the equivalence point? Select a good indicator for this titration from Table 17.7.

***17.118** What is the pH of a solution prepared by mixing 25.0 mL of 0.180 *M* $HC_2H_3O_2$ with 40.0 mL of 0.250 *M* NaOH?

***17.119** What is the pH of a solution prepared by mixing exactly 25.0 mL of 0.200 *M* $HC_2H_3O_2$ with 15.0 mL of 0.400 *M* KOH?

***17.120** For the titration of 75.00 mL of 0.1000 *M* acetic acid with 0.1000 *M* NaOH, calculate the pH **(a)** before the addition of any NaOH solution, **(b)** after 25.00 mL of the base has been added, **(c)** after half of the $HC_2H_3O_2$ has been neutralized, and **(d)** at the equivalence point.

***17.121** For the titration of 50.00 mL of 0.1000 *M* ammonia with 0.1000 *M* HCl, calculate the pH **(a)** before the addition of any HCl solution, **(b)** after 20.00 mL of the acid has been added, **(c)** after half of the NH_3 has been neutralized, and **(d)** at the equivalence point.

Additional Exercises

***17.122** Calculate the percentage ionization of acetic acid in solutions having concentrations of 1.0 *M*, 0.10 *M*, and 0.010 *M*. How does the percentage ionization of a weak acid change as the acid becomes more dilute?

17.123 What is the pH of a solution that is 0.100 *M* in HCl and also 0.125 *M* in $HC_2H_3O_2$? What is the concentration of acetate ion in this solution?

17.124 A solution is prepared by mixing 325 mL of 0.500 *M* NH_3 and 175 mL of 0.500 *M* HCl. Assuming that the volumes are additive, what is the pH of the resulting mixture?

***17.125** A solution is prepared by dissolving 15.0 g of pure $HC_2H_3O_2$ and 25.0 g of $NaC_2H_3O_2$ in 775 mL of solution (the final volume). **(a)** What is the pH of the solution? **(b)** What would the pH of the solution be if 25.0 mL of 0.250 *M* NaOH were added? **(c)** What would the pH be if 25.0 mL of 0.40 *M* HCl were added to the original 775 mL of buffer solution?

***17.126** For an experiment involving what happens to the growth of a particular fungus in a slightly acidic medium, a biochemist needs 255 mL of an acetate buffer with a pH of 5.12. The buffer solution has to be able to hold the pH to within ±0.10 pH unit of 5.12 even if 0.0100 mol of NaOH or 0.0100 mol of HCl enters the solution.

(a) What is the minimum number of grams of acetic acid and of sodium acetate dihydrate that must be used to prepare the buffer?

(b) Describe the buffer by giving its molarity in acetic acid and its molarity in sodium acetate.

(c) What is the pH of an unbuffered solution made by adding 0.0100 mol of NaOH to 255 mL of pure water?

(d) What is the pH of an unbuffered solution made by adding 0.0100 mol of HCl to 255 mL of pure water?

***17.127** Predict whether the pH of 0.120 *M* NH_4CN is greater than, less than, or equal to 7.00. Give your reasons.

***17.128** What is the pH of a 4.5×10^{-2} *M* solution of ammonium acetate, $NH_4C_2H_3O_2$?

***17.129** How many milliliters of ammonia gas measured at 25.2 °C and 745 torr must be dissolved in 0.250 L of 0.050 *M* HNO_3 to give a solution with a pH of 9.26?

17.130 $HClO_4$ is a stronger proton donor than HNO_3, but in water both acids appear to be of equal strength; they are both 100% ionized. Why is this so? What solvent property would be necessary in order to distinguish between the acidities of these two Brønsted acids?

17.131 The hydrogen sulfate ion, HSO_4^-, is a moderately strong Brønsted acid with a K_a of 1.2×10^{-2}.

(a) Write the chemical equation for the ionization of the acid and give the appropriate K_a expression.

(b) What is the value of $[H^+]$ in 0.010 *M* HSO_4^- (furnished by the salt, $NaHSO_4$)? Do NOT make simplifying assumptions; use the quadratic equation.

(c) What is the calculated $[H^+]$ in 0.010 M HSO_4^-, obtained by using the usual simplifying assumption?

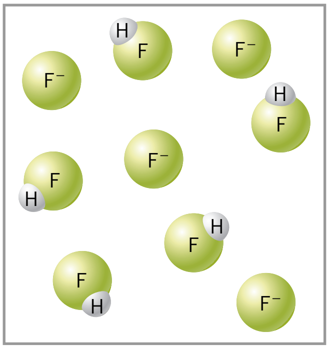
(d) How much error is introduced by incorrectly using the simplifying assumption?

17.132 Some people who take megadoses of ascorbic acid will drink a solution containing as much as 6.0 g of ascorbic acid dissolved in a glass of water. Assuming the volume to be 0.250 L, calculate the pH of this solution.

17.133 For the titration of 25.00 mL of 0.1000 M HCl with 0.1000 M NaOH, calculate the pH of the reaction mixture after each of the following total volumes of base have been added to the original solution. (Remember to take into account the change in total volume.) Construct a graph showing the titration curve for this experiment.

(a) 0 mL
(b) 10.00 mL
(c) 24.90 mL
(d) 24.99 mL
(e) 25.00 mL
(f) 25.01 mL
(g) 25.10 mL
(h) 26.00 mL
(i) 50.00 mL

17.134 Below is a diagram illustrating a mixture HF and F^- in an aqueous solution. For this mixture, does pH equal pK_a for HF? Explain. Describe how the number of HF molecules and F^- ions will change after three OH^- ions are added. How will the number of HF and F^- change if two H^+ ions are added? Explain your answers by using chemical equations.



Multi-Concept Problems

17.135 How many milliliters of 0.10 M NaOH must be added to 0.200 L of 0.010 M HCl to give a mixture with a pH of 3.00?

17.136 Milk of magnesia is a suspension of magnesium hydroxide in water. Although $Mg(OH)_2$ is relatively insoluble, a small amount does dissolve in the water, which makes the mixture slightly basic and gives it a pH of 10.08. How many grams of $Mg(OH)_2$ are actually dissolved in 2.0 tablespoons of milk of magnesia?

17.137 How many milliliters of 0.0100 M KOH are needed to completely neutralize the HCl in 325 mL of a hydrochloric acid solution that has a pH of 2.25?

17.138 It was found that 25.20 mL of an HNO_3 solution are needed to react completely with 30.0 mL of a LiOH solution that has a pH of 12.05. What is the molarity of the HNO_3 solution?

***17.139** Suppose 38.0 mL of 0.000200 M HCl is added to 40.0 mL of 0.000180 M NaOH. What will be the pH of the final mixture?

***17.140** Suppose 10.0 mL of HCl gas at 25 °C and 734 torr is bubbled into 257 mL of pure water. What will be the pH of the resulting solution, assuming all the HCl dissolves in the water?

***17.141** Suppose the HCl described in the preceding problem is bubbled into 20.00 L of a solution of NaOH that has a pH of 10.50. What will the pH of the resulting solution be?

***17.142** What is the approximate freezing point of a 0.50 M solution of dichloroacetic acid, $HC_2HO_2Cl_2$ ($K_a = 5.0 \times 10^{-2}$)? Assume the density of the solution is 1.0 g/mL.

Exercises in Critical Thinking

17.143 What happens to the pH of a solution as it is heated? Does that mean that the autoionization of water is exothermic or endothermic?

17.144 Can the pH of a solution ever have a negative value? Give an example of a situation where the pH has a negative value.

***17.145** In simplifying our calculations, we were satisfied with a maximum error of 5% in the concentration of hydronium ions when we compare the value calculated from the quadratic formula to the value obtained using simplifying assumptions. What does an error of 5% in hydrogen ion concentration mean in terms of pH? Is the pH error the same for a $1.0 \times 10^{-3}\ M\ \mathrm{H}^+$ solution as it is for a $5.0 \times 10^{-6}\ M$ solution?

17.146 In the 1950s it was discovered that lakes in the northeastern United States had declining fish populations due to increased acidity. In order to address the problem of lake acidification, make a list of what you need to know in order to start addressing the problem.

17.147 Where are buffers found in everyday consumer products? Propose reasons why a manufacturer would use a buffer in a given product of your choice.

17.148 Why must the acid used for a buffer have a $\mathrm{p}K_\mathrm{a}$ within one pH unit of the pH of the buffer? What happens if that condition is not met?

17.149 What conjugate acid–base pairs are used to buffer **(a)** over-the-counter drugs, **(b)** foods, **(c)** cosmetics, and **(d)** shampoos?

17.150 Your blood at 37 °C needs to be maintained within a narrow pH range of 7.35 to 7.45 to maintain optimal health. What possible conjugate acid–base pairs are present in blood that can buffer the blood and keep it within this range?

17.151 Develop a list of the uses of phosphoric acid in various consumer products.

17.152 Investigate the salts of phosphoric acid (i.e., those that contain $H_2PO_4^{-}$, HPO_4^{2-}, and PO_4^{3-}) to find out how they are used in consumer products.

17.153 What would our pH scale look like if Arrhenius decided that $\mathrm{pH} = -\ln\,[\mathrm{H}^+]$? What would the pH of a neutral solution be?

18 Solubility and Simultaneous Equilibria

Chapter Outline

18.1 | Equilibria in Solutions of Slightly Soluble Neutral Salts

18.2 | Equilibria in Solutions of Metal Oxides and Sulfides

18.3 | Selective Precipitation

18.4 | Equilibria Involving Complex Ions

18.5 | Complexation and Solubility

Many beautiful statues that have graced New York City are slowly eroding away. This statue was carved from limestone, which is composed largely of calcium carbonate. Calcium carbonate is insoluble in water, but the solubility of it increases with increasing acidity. As the rain in America became more acidic in the past century, these statues have begun to diappear. In this chapter, we will discuss the solubility equilibria of "insoluble" salts such as calcium carbonate, and how these equilibria can be disrupted by acids and bases. © 1994 NYC Parks Photo Archive/Fundamental Photographs; © 1994 Kristen Brochmann/Fundamental Photographs.

This Chapter in Context

In the preceding chapters you learned how the principles of equilibrium can be applied to aqueous solutions of acids and bases. In this chapter we extend these principles to aqueous reactions that involve the formation and dissolving of precipitates (a topic we introduced in Chapter 5). Many such reactions are common in the world around us. For example, groundwater rich in carbon dioxide dissolves deposits of calcium carbonate, producing vast underground caverns, and as the remaining calcium-containing solution gradually evaporates, stalactites and stalagmites form. Within living organisms, precipitation reactions form the hard calcium carbonate shells of clams, oysters, and coral, as well as the unwanted calcium oxalate and calcium phosphate deposits we call kidney stones. Also, dilute acids in our mouths promote the dissolving of tooth enamel, which is composed of a mineral made up of calcium phosphate and calcium hydroxide.

In this chapter you will learn how we can calculate the solubilities of "insoluble" salts in water and in other solutions, and how the formation of substances called complex ions can affect solubilities. The concepts we develop here can tell us when precipitates will form and when they will dissolve, and we can use these in a practical lab setting in the separation of metal ions for chemical analysis.

18.1 | Equilibria in Solutions of Slightly Soluble Neutral Salts

Solubility Product Constant, K_{sp}

None of the salts we described in Chapter 5 as being insoluble are *totally* insoluble. For example, the solubility rules tell us that AgCl is "insoluble," but if some solid AgCl is placed in water, a very small amount does dissolve. Once the solution has become saturated, the following equilibrium is established between the undissolved AgCl and its ions in the solution:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

(In a saturated solution of AgCl)

■ Recall that when salts go into solution, they dissociate essentially completely, so the equilibrium is between the solid and the ions that are in the solution.

This is a heterogeneous equilibrium because it involves a solid reactant (AgCl) in equilibrium with ions in aqueous solution. Using the procedure developed in Section 15.4 (page 706), we write the equilibrium law as shown in Equation 18.1, omitting the solid from the mass action expression.

$$[\mathrm{Ag}^+][\mathrm{Cl}^-] = K_{sp} \tag{18.1}$$

The equilibrium constant, K_{sp}, is called the **solubility product constant** (because the system is a *solubility* equilibrium and the *constant* equals a *product* of ion concentrations).

TOOLS

Solubility product constant, K_{sp}

It's important that you understand the distinction between solubility and solubility product. The *solubility* of a salt is the amount of the salt that dissolves in a given amount of solvent to give a saturated solution. The *solubility product* is the product of the molar concentrations of the ions in the saturated solution, raised to appropriate powers (see below).

The solubilities of salts change with temperature, so a value of K_{sp} applies only at the temperature at which it was determined. Some typical K_{sp} values are listed in Table 18.1 and in Appendix C.

Table 18.1 Solubility Product Constants[a]

Type	Salt		Ions of Salt	K_{sp} (25 °C)
Halides	CaF_2	$\rightleftharpoons$	$Ca^{2+} + 2F^-$	3.4×10^{-11}
	PbF_2	$\rightleftharpoons$	$Pb^{2+} + 2F^-$	3.3×10^{-8}
	$AgCl$	$\rightleftharpoons$	$Ag^+ + Cl^-$	1.8×10^{-10}
	$AgBr$	$\rightleftharpoons$	$Ag^+ + Br^-$	5.4×10^{-13}
	AgI	$\rightleftharpoons$	$Ag^+ + I^-$	8.5×10^{-17}
	$PbCl_2$	$\rightleftharpoons$	$Pb^{2+} + 2Cl^-$	1.7×10^{-5}
	$PbBr_2$	$\rightleftharpoons$	$Pb^{2+} + 2Br^-$	6.6×10^{-6}
	PbI_2	$\rightleftharpoons$	$Pb^{2+} + 2I^-$	9.8×10^{-9}
Hydroxides	$Al(OH)_3$	$\rightleftharpoons$	$Al^{3+} + 3OH^-$	3×10^{-34} (b)
	$Ca(OH)_2$	$\rightleftharpoons$	$Ca^{2+} + 2OH^-$	5.0×10^{-6}
	$Fe(OH)_2$	$\rightleftharpoons$	$Fe^{2+} + 2OH^-$	4.9×10^{-17}
	$Fe(OH)_3$	$\rightleftharpoons$	$Fe^{3+} + 3OH^-$	2.8×10^{-39}
	$Mg(OH)_2$	$\rightleftharpoons$	$Mg^{2+} + 2OH^-$	5.6×10^{-12}
	$Zn(OH)_2$	$\rightleftharpoons$	$Zn^{2+} + 2OH^-$	3×10^{-17} (c)
Carbonates	Ag_2CO_3	$\rightleftharpoons$	$2Ag^+ + CO_3^{2-}$	8.5×10^{-12}
	$MgCO_3$	$\rightleftharpoons$	$Mg^{2+} + CO_3^{2-}$	6.8×10^{-8}
	$CaCO_3$	$\rightleftharpoons$	$Ca^{2+} + CO_3^{2-}$	3.4×10^{-9} (d)
	$SrCO_3$	$\rightleftharpoons$	$Sr^{2+} + CO_3^{2-}$	5.6×10^{-10}
	$BaCO_3$	$\rightleftharpoons$	$Ba^{2+} + CO_3^{2-}$	2.6×10^{-9}
	$CoCO_3$	$\rightleftharpoons$	$Co^{2+} + CO_3^{2-}$	1.0×10^{-10}
	$NiCO_3$	$\rightleftharpoons$	$Ni^{2+} + CO_3^{2-}$	1.4×10^{-7}
	$ZnCO_3$	$\rightleftharpoons$	$Zn^{2+} + CO_3^{2-}$	1.5×10^{-10}
Chromates	Ag_2CrO_4	$\rightleftharpoons$	$2Ag^+ + CrO_4^{2-}$	1.1×10^{-12}
	$PbCrO_4$	$\rightleftharpoons$	$Pb^{2+} + CrO_4^{2-}$	1.8×10^{-14} (e)
Sulfates	$CaSO_4$	$\rightleftharpoons$	$Ca^{2+} + SO_4^{2-}$	4.9×10^{-5}
	$SrSO_4$	$\rightleftharpoons$	$Sr^{2+} + SO_4^{2-}$	3.4×10^{-7}
	$BaSO_4$	$\rightleftharpoons$	$Ba^{2+} + SO_4^{2-}$	1.1×10^{-10}
	$PbSO_4$	$\rightleftharpoons$	$Pb^{2+} + SO_4^{2-}$	2.5×10^{-8}
Oxalates	CaC_2O_4	$\rightleftharpoons$	$Ca^{2+} + C_2O_4^{2-}$	2.3×10^{-9}
	MgC_2O_4	$\rightleftharpoons$	$Mg^{2+} + C_2O_4^{2-}$	4.8×10^{-6}
	BaC_2O_4	$\rightleftharpoons$	$Ba^{2+} + C_2O_4^{2-}$	1.2×10^{-7}
	FeC_2O_4	$\rightleftharpoons$	$Fe^{2+} + C_2O_4^{2-}$	2.1×10^{-7}
	PbC_2O_4	$\rightleftharpoons$	$Pb^{2+} + C_2O_4^{2-}$	2.7×10^{-11}

[a] Data are for 25 °C. See *Handbook of Chemistry and Physics*, 87th Ed., O. R. Lider, Editor, CRC Press.
[b] Alpha form. [c] Amorphous form. [d] Calcite form. [e] At 10 °C.

Ion Product, the Reaction Quotient for Slightly Soluble Salts

In preceding chapters we described the value of the mass action expression as the reaction quotient, Q. For simple solubility equilibria like those discussed in this section, the mass action expression is a product of ion concentrations raised to appropriate powers, so Q is often called the **ion product** of the salt. Thus, for AgCl,

$$\text{ion product} = [Ag^+][Cl^-] = Q$$

At any dilution of a salt throughout the range of possibilities for an *unsaturated* solution, there will be varying values for the ion concentrations and, therefore, for Q. However, Q acquires a constant value, K_{sp}, in a *saturated* solution. When a solution is less than saturated, the value of Q is less than K_{sp}. Thus, we can use the numerical value of Q for a given solution as a test for saturation by comparing it to the value of K_{sp}.

Many salts produce more than one of a given ion per formula unit when they dissociate, and this introduces exponents into the ion product expression. For example, when silver chromate, Ag_2CrO_4, precipitates (Figure 18.1), it enters into the following solubility equilibrium:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

The equilibrium law is obtained following the procedure we developed in Chapter 15, using coefficients as exponents in the mass action expression:

$$[Ag^+]^2[CrO_4^{2-}] = K_{sp}$$

Thus, the ion product contains the ion concentrations raised to powers equal to the number of ions released per formula unit. This means that to obtain the correct ion product expression you have to know the formulas of the ions that make up the salt. In other words, you have to realize that Ag_2CrO_4 is composed of $2Ag^+$ and the polyatomic anion CrO_4^{2-}. If necessary, review the list of polyatomic ions in Table 3.5 on page 84.

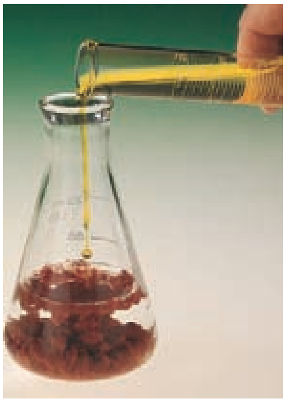


Figure 18.1 | **Silver chromate.** When sodium chromate is added to a solution of silver nitrate, deep red-brown "insoluble" silver chromate, Ag_2CrO_4, precipitates. *(Michael Watson)*

Practice Exercises

18.1 | Write the equation for the equilibrium involved in the solubility of barium phosphate, $Ba_3(PO_4)_2$, and write the equilibrium law corresponding to K_{sp}. (*Hint*: Remember that it's a heterogeneous equilibrium.)

18.2 | What are the ion product expressions for the following salts? (a) calcium oxalate, (b) silver sulfate.

Determining K_{sp} from Molar Solubilities

One way to determine the value of K_{sp} for a salt is to measure its solubility—that is, how much of the salt is required to give a saturated solution in a specified amount of solution. It is useful to express this as the **molar solubility**, which equals *the number of moles of salt dissolved in one liter of its* ***saturated solution.*** The molar solubility can be used to calculate the K_{sp} under the assumption that all of the salt that dissolves is 100% dissociated into the ions implied in the salt's formula.[1]

TOOLS Molar solubility

One note here about calculations involving solubility products. Many of the calculations we will carry out include changes in concentration, and the use of concentration tables, as introduced in Chapter 15, will help organize our thoughts and make the calculations easier. If used properly, the concentration tables lay out all of the values for the concentrations and changes that occur during the solubility process. This is illustrated in Example 18.1.

TOOLS Concentration tables

Example 18.1
Calculating K_{sp} from Solubility Data

Silver bromide, AgBr, is the light-sensitive compound used in nearly all photographic film. The solubility of AgBr in water was measured to be 1.3×10^{-4} g L^{-1} at 25 °C. Calculate K_{sp} for AgBr at this temperature.

---

[1] This assumption works reasonably well for slightly soluble salts made up of singly charged ions, like silver bromide. For simplicity, and to illustrate the nature of calculations involving solubility equilibria, we will work on the assumption that *all* salts behave as though they are 100% dissociated. This is not entirely true, especially for salts of multiply charged ions, so the accuracy of our calculations is limited. We discussed the reasons for the incomplete dissociation of salts in Section 13.7.

■ **Analysis:** For any question about the solubility of a slightly soluble salt, we need to start with the balanced chemical equation, from which we construct the equation for the solubility product constant, K_{sp}.

In order to determine the K_{sp}, we will need the molar solubilities of the ions that are in solution. We are given a solubility of AgBr in g L^{-1}, so we will have to convert the concentration of each ion to mol L^{-1}. We also need to keep track of how many ions AgBr gives in solution, which we can get from the stoichiometric ratio in the balanced chemical equation.

Using the concentrations of the ions in solution, we can calculate the K_{sp} using the equilibrium equation.

■ **Assembling the Tools:** The first tool that we will need is the equation for the solubility product constant, K_{sp}, which we derived from the balanced chemical equation:

$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Br}^{-}(aq) \qquad K_{sp} = [\mathrm{Ag}^{+}][\mathrm{Br}^{-}]$$

To calculate K_{sp}, we need the concentrations of the ions expressed in moles per liter, so we will use the tools from Chapter 4 to convert the mass to moles in order to convert 1.3×10^{-4} g L^{-1} to moles per liter.

For many problems dealing with solubility, the concentration table is a useful tool. We introduced this tool in Chapter 15, and it is helpful to review its use again here. The first row, the initial concentration row, is where we put the concentrations of ions before any reaction occurs, and in this case, that means the concentrations before any of the solid dissolves. The second row is for the changes in concentration, which, for this example, will be the concentration of ions in moles per liter. The final row, the equilibrium concentration row, is the sum of the first two rows.

The equilibrium concentrations are now used to calculate the value of K_{sp} by applying the concentrations to the K_{sp} equation.

■ **Solution:** We need to start with the balanced chemical equation and the expression for the solubility product constant,

$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Br}^{-}(aq)$$
$$K_{sp} = [\mathrm{Ag}^{+}][\mathrm{Br}^{-}]$$

Then we calculate the number of moles of AgBr dissolved per liter:

$$\text{molar solubility} = \frac{1.3 \times 10^{-4}\ \cancel{\text{g AgBr}}}{1.00\ \text{L soln}} \times \frac{1.00\ \text{mol AgBr}}{187.77\ \cancel{\text{g AgBr}}} = 6.9 \times 10^{-7}\ \text{mol L}^{-1}$$

Now we can begin to set up the concentration table, which is shown below. Notice first that there are no entries in the "reactant" column. This is because AgBr is a solid and doesn't appear in the mass action expression.

In setting up the table, it is helpful if we imagine the formation of the saturated solution to occur stepwise. Once we have the equilibrium ion concentrations, we substitute them into the ion product expression to calculate K_{sp}.

Initial Concentrations

In the first row under the formulas of the ions—the initial concentration row—we enter the initial concentrations of Ag^{+} and Br^{-}. *Remember, these are the concentrations of the ions present in the solvent before any of the AgBr dissolves.* In this case, the solvent is pure water. Neither Ag^{+} nor Br^{-} are present in pure water, so we set the initial concentrations equal to zero. However, if the solvent had contained a solute that is a source of one of the ions in the equilibrium, we would have used its concentration as the initial concentration of that ion.

Changes in Concentrations

In the "change" row, we enter data on how the concentrations of the $Ag^{+}(aq)$ and $Br^{-}(aq)$ change when the AgBr dissolves. Because dissolving the salt always increases these concentrations, these entries are always positive. They are also related to each other by the stoichiometry of the dissociation reaction. Thus, when AgBr dissolves, Ag^+ and Br^- ions are released in a 1:1 ratio. So, when 6.9×10^{-7} mol of AgBr dissolves (per liter), 6.9×10^{-7} mol of Ag^+ ion and 6.9×10^{-7} mol of Br^- ion go into solution. The concentrations of these species thus *change* (increase) by these amounts.

Equilibrium Concentrations

As usual, we obtain the equilibrium values by adding the "initial concentrations" to the "changes."

	$AgBr(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+$	$Br^-(aq)$
Initial concentrations (*M*)	No entries in this column		0		0
Changes in concentrations when AgBr dissolves (*M*)			$+6.9 \times 10^{-7}$		$+6.9 \times 10^{-7}$
Equilibrium concentrations (*M*)			6.9×10^{-7}		6.9×10^{-7}

There are no entries in the column under AgBr(*s*) because this substance does not appear in the K_{sp} expression.

We now substitute the equilibrium ion concentrations into the K_{sp} expression.

$$\begin{aligned} K_{sp} &= [Ag^+][Br^-] \\ &= (6.9 \times 10^{-7})(6.9 \times 10^{-7}) \\ &= 4.8 \times 10^{-13} \end{aligned}$$

The K_{sp} of AgBr is thus calculated to be 4.8×10^{-13} at 25 °C.

Is the Answer Reasonable? We can check this problem by approximating the molar mass of AgBr following the calculations, and by checking our reasoning. We've divided 1.3×10^{-4} by a number that's approximately 200, which would give a value of about 6.5×10^{-7}, so our molar solubility seems reasonable. (Also, AgBr has a very low solubility in water, so we expect the molar solubility to be very small.) The reasoning involved in the change row also makes sense; the number of moles of ions formed per liter must each equal the number of moles of AgBr that dissolve. Finally, if we round 6.9×10^{-7} to 7×10^{-7} and square it, we obtain $49 \times 10^{-14} = 4.9 \times 10^{-13}$. Our answer of 4.8×10^{-13}, therefore, seems to be okay.

The K_{sp} we calculated from the solubility data here differs by only 4% from the value in Table 18.1.

Example 18.2
Calculating K_{sp} from Molar Solubility Data

The molar solubility of silver chromate, Ag_2CrO_4, in water is 6.7×10^{-5} mol L^{-1} at 25 °C. What is K_{sp} for Ag_2CrO_4?

Analysis: This problem is very similar to Example 18.1, except that the ions are not in a one-to-one ratio. In this case, when Ag_2CrO_4 dissolves, it produces two Ag^+ for each Ag_2CrO_4.

Assembling the Tools: The tools we will need for this problem are the same as the tools in Example 18.1, except we are given the solubility in mol L^{-1}, so we do not have to convert from grams to moles. We will need the balanced equilibrium equation and the K_{sp} expression:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

We will also use the concentration table as our tool for analyzing the concentrations. We will use it in the same fashion as we did in Example 18.1. However, we need to be careful with the ions—there will be two moles of silver ions for each mole of Ag_2CrO_4—so when we calculate the moles of silver dissolved, we have to use the mole ratio of 2 mol Ag^+ to 1 mol Ag_2CrO_4.

Solution: For the balanced equilibrium equation and K_{sp} expression, we have

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

The solute is pure water, so neither Ag^+ nor CrO_4^{2-} is present before the salt dissolves; their initial concentrations are zero. For the "change" row, we have to be careful to take into account the formula of the salt. In a liter of water, when 6.7×10^{-5} mol of Ag_2CrO_4 dissolves, we obtain 6.7×10^{-5} mol of CrO_4^{2-} and $2 \times (6.7 \times 10^{-5}$ mol) of Ag^+. With this information, we can fill in the "initial" and "change" rows. Then, we can add the "initial" and "change" rows together to arrive at the equilibrium concentrations.

$Ag_2CrO_4(s)$ $\rightleftharpoons$	$2Ag^+(aq)$	+	$CrO_4^{2-}(aq)$
Initial concentrations (*M*)	0		0
Changes in concentrations when Ag_2CrO_4 dissolves (*M*)	$+[2 \times (6.7 \times 10^{-5})]$ $= +1.3 \times 10^{-4}$		$+6.7 \times 10^{-5}$
Equilibrium concentrations (*M*)	1.3×10^{-4}		6.7×10^{-5}

Substituting the equilibrium concentrations into the mass action expression for K_{sp} gives

$$\begin{aligned} K_{sp} &= (1.3 \times 10^{-4})^2(6.7 \times 10^{-5}) \\ &= 1.1 \times 10^{-12} \end{aligned}$$

So the K_{sp} of Ag_2CrO_4 at 25 °C is calculated to be 1.1×10^{-12}.

Is the Answer Reasonable? The critical link in solving the problem correctly is placing the correct quantities in the "initial" and "change" rows. The Ag_2CrO_4 is dissolved in water, so the initial concentrations of the ions must be zero; these entries are okay. For the "changes," it's important to remember that the quantities are related to each other by the coefficients in the balanced chemical equation. That means the change for Ag^+ must be twice as large as the change for CrO_4^{2-}. Studying the table, we see that we've done this correctly. We can also see that we've added the "change" to the "initial" values correctly, and that we've performed the proper arithmetic in evaluating the mass action expression.

Practice Exercises

18.3 | The solubility of thallium(I) iodide, TlI, in water at 20 °C is 5.9×10^{-3} g L^{-1}. Using this fact, calculate K_{sp} for TlI on the assumption that it is 100% dissociated in the solution. (*Hint*: What is the molar solubility of TlI?)

18.4 | One liter of water will dissolve 2.15×10^{-3} mol of PbF_2 at 25 °C. Calculate the value of K_{sp} for PbF_2.

18.5 | The slightly soluble salt, Ag_3PO_4, has a solubility of 7.5×10^{-3} g L^{-1} at 25 °C. Assuming that the ions completely dissociate in solution, calculate the value of K_{sp} for Ag_3PO_4.

Determining Molar Solubility from K_{sp}

Besides calculating K_{sp} from solubility information, we can also compute solubilities from values of K_{sp}. Examples 18.3 and 18.4 illustrate the calculations.[2]

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[2] As noted earlier, these calculations ignore the fact that the salt that dissolves is not truly 100% dissociated into the ions implied in the salt's formula. This is particularly a problem with the salts of multiply charged ions, so the solubilities of such salts, when calculated from their K_{sp} values, must be taken as rough estimates. In fact, many calculations involving K_{sp} give values that are merely estimates.

Example 18.3

Calculating Molar Solubility from K_{sp}

What is the molar solubility of AgCl in pure water at 25 °C?

Analysis: To solve the problem, we're going to need a balanced chemical equation for the solubility equilibrium, the equilibrium law (K_{sp} expression), and the value of K_{sp}, which we can obtain from Table 18.1. We will also need to set up a concentration table, but this time the solubility is unknown, so this will affect the quantities we enter into the change row.

Assembling the Tools: The relevant equations to solve this problem are

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \qquad K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

With these equations, we can build a concentration table. First, we see that the solvent is pure water, so neither Ag^+ nor Cl^- is present in solution at the start; their *initial* concentrations are zero.

Next, we turn to the "change" row. If we knew what the changes were, we could calculate the equilibrium concentrations and figure out the molar solubility. But we don't know the changes, so we will have to find them algebraically. To do this, *we will define our unknown x as the molar solubility of the salt*—that is, the number of moles of AgCl that dissolves in one liter. Because 1 mol of AgCl yields 1 mol Ag^+ and 1 mol Cl^-, the concentration of each of these ions increases by x (i.e., their changes are each $+x$).

Solution: Our concentration table is as follows:

$\text{AgCl}(s) \rightleftharpoons$	$\text{Ag}^+(aq)$	+	$\text{Cl}^-(aq)$
Initial concentrations (M)	0		0
Changes in concentrations when AgCl dissolves (M)	$+x$		$+x$
Equilibrium concentrations (M)	x		x

■ By defining x as the molar solubility, the coefficients of x in the "change" row are the same as the coefficients of Ag^+ and Cl^- in the equation for the equilibrium.

We make the substitutions into the K_{sp} expression, using equilibrium quantities from the last row of the table:

$$(x)(x) = 1.8 \times 10^{-10}$$
$$x = 1.3 \times 10^{-5}$$

The calculated molar solubility of AgCl in water at 25 °C is 1.3×10^{-5} mol L^{-1}.

Is the Answer Reasonable? The solvent is water, so the initial concentrations are zero. If x is the molar solubility, then the changes in the concentrations of Ag^+ and Cl^- when the salt dissolves must also be equal to x. We can also check the algebra, which we've done correctly, so the answer seems to be okay.

Example 18.4

Calculating Molar Solubility from K_{sp}

Calculate the molar solubility of lead(II) iodide in water at 25 °C from its K_{sp}.

Analysis: The key to this problem is realizing that there are two iodide ions released for each lead(II) iodide. For this problem, we will need to start with PbI_2, the formula for lead(II) iodide, so that we can set up the balanced chemical equation and the K_{sp} expression. Then, we will need to use a concentration table to find the molar solubilities of the lead(II) iodide.

A precipitate of yellow PbI_2 forms when the two colorless solutions, one with sodium iodide and the other of lead(II) nitrate, are mixed. *(Lawrence Migdale/Photo Researchers)*

Assembling the Tools: The tools are the same tools we used in Example 18.3, except that the first thing we need to do is determine the formula for lead(II) iodide, PbI_2, which is obtained from the rules of nomenclature in Chapter 3. We then use the equation for the equilibrium and the K_{sp} expression. We obtain K_{sp} from Table 18.1.

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \qquad K_{sp} = [Pb^{2+}][I^-]^2 = 9.8 \times 10^{-9}$$

For the concentration table, we can start with the solvent, water, and the initial concentrations of the ions, which are zero. As before, we will define x as the molar solubility of the salt. By doing this, the coefficients of x in the "change" row will be identical to the coefficients of the ions in the chemical equation. This assures us that the changes in the concentrations are in the correct mole ratio.

Solution: Here is the concentration table.

$PbI_2(s) \rightleftharpoons$	$Pb^{2+}(aq)$	$+\ 2I^-(aq)$
Initial concentrations (M)	0	0
Changes in concentrations when PbI_2 dissolves (M)	$+x$	$+2x$
Equilibrium concentrations (M)	x	$2x$

Substituting equilibrium quantities into the K_{sp} expression gives

$$\begin{aligned} K_{sp} = (x)(2x)^2 = 4x^3 &= 9.8 \times 10^{-9} \\ x^3 &= 2.5 \times 10^{-9} \\ x &= 1.3 \times 10^{-3} \end{aligned}$$

Thus, the molar solubility of PbI_2 in pure water is calculated to be 1.3×10^{-3} mol L^{-1}.

Is the Answer Reasonable? We check the entries in the table. The solvent is water, so the initial concentrations are equal to zero. By setting x equal to the moles per liter of PbI_2 that dissolves (i.e., the molar solubility), the coefficients x in the "change" row have to be the same as the coefficients of Pb^{2+} and Cl^- in the balanced chemical equation. The entries in the "change" row are okay. In performing the algebra, notice that when we square $2x$, we get $4x^2$. Multiplying $4x^2$ by x gives $4x^3$. After that, if our math is correct, the answer is correct.

Practice Exercises

18.6 | What is the calculated molar solubility in water at 25 °C of (a) AgBr and (b) Ag_2CO_3? (*Hint*: Review the algebra in Example 18.4.)

18.7 | Calculate the molar solubility of $Ca_3(PO_4)_2$ in water. Its K_{sp} is 2.1×10^{-33}.

The Common Ion Effect

Suppose that we stir some lead(II) chloride (a compound having a low solubility) with water long enough to establish the following equilibrium:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

If we now add a concentrated solution of a soluble lead compound, such as $Pb(NO_3)_2$, the increased concentration of Pb^{2+} in the $PbCl_2$ solution will drive the position of equilibrium to the left, causing some $PbCl_2$ to precipitate. The phenomenon is simply an application of Le Châtelier's principle, the net result being that $PbCl_2$ is less soluble in a solution that contains Pb^{2+} from another source than it is in pure water. The same effect is produced if a concentrated solution of a soluble chloride salt such as NaCl is added to the saturated $PbCl_2$ solution. The added Cl^- will drive the equilibrium to the left, reducing the amount of dissolved $PbCl_2$.

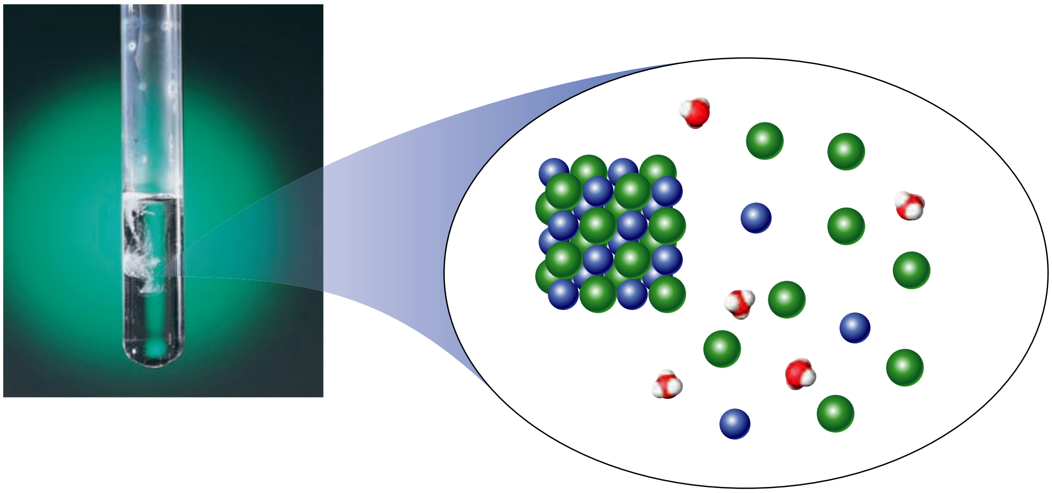

Figure 18.2 | **The common ion effect.** The test tube shown here initially held a saturated solution of NaCl, where the equilibrium, $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$, had been established. Addition of a few drops of concentrated HCl, containing a high concentration of the common ion Cl^-, in green, forced the equilibrium to shift to the left. This caused some white crystals of solid NaCl to precipitate. *(Michael Watson)*

The phenomenon we just described is an example of the *common ion effect*, which we also described in Chapter 17. In this case, Pb^{2+} is the common ion when we add $Pb(NO_3)_2$ and Cl^- is the common ion when we add NaCl. Figure 18.2 shows how even a relatively soluble salt, NaCl, can be forced out of its saturated solution simply by adding concentrated hydrochloric acid, which serves as a source of the common ion, Cl^-. The common ion effect can dramatically lower the solubility of a salt, as Example 18.5 demonstrates.

Example 18.5
Calculations Involving the Common Ion Effect

What is the molar solubility of PbI_2 in a 0.10 M NaI solution?

Analysis: Because PbI_2 and NaI have the same ion in common, this is an example of a calculation involving the common ion effect. As usual, to solve the problem we're going to need a balanced chemical equation for the solubility equilibrium, the equilibrium law (i.e., the K_{sp} expression), and the value of K_{sp}, which is listed in Table 18.1. We will also need to set up a concentration table as in Example 18.4, but this time we have to take into account the solute already present in the solution.

Assembling the Tools: We begin with the balanced chemical equation for the equilibrium, the appropriate K_{sp} expression, and the value of K_{sp} obtained from Table 18.1:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \qquad K_{sp} = [Pb^{2+}][I^-]^2 = 9.8 \times 10^{-9}$$

As before, we imagine that we are adding the PbI_2 to a solvent into which it dissolves. This time, however, the solvent isn't water; it's a solution of NaI, which contains one of the ions of the salt PbI_2. The NaI completely dissociates and yields 0.10 M Na^+ and 0.10 M I^-. The initial concentration of I^- is therefore 0.10 M.

Next, we let x be the molar solubility of PbI_2. When x mol of PbI_2 dissolves per liter, the concentration of Pb^{2+} changes by $+x$ and that of I^- by twice as much, or $+2x$. Finally, the equilibrium concentrations are obtained by summing the initial concentrations and the changes.

Solution: Here is the concentration table.

	$PbI_2(s) \rightleftharpoons$	$Pb^{2+}(aq)$	+	$2I^-(aq)$
Initial concentrations (M)		0		0.10
Changes in concentrations when PbI_2 dissolves (M)		$+x$		$+2x$
Equilibrium concentrations (M)		x		$0.10 + 2x$

Substituting equilibrium values into the K_{sp} expression gives

$$K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.10 + 2x)^2 = 9.8 \times 10^{-9}$$

Just a brief inspection reveals that solving this expression for x will be difficult if we cannot simplify the math. Fortunately, a simplification is possible, because the small value of K_{sp} for PbI_2 indicates that the salt has a very low solubility. This means very little of the salt will dissolve, so x (or even $2x$) will be quite small. Let's assume that $2x$ will be much smaller than 0.10. If this is so, then

$$0.10 + 2x \approx 0.10 \text{ (assuming } 2x \text{ is negligible compared to 0.10)}$$

Substituting 0.10 M for the I^- concentration gives

$$\begin{aligned} K_{sp} &= (x)(0.10)^2 = 9.8 \times 10^{-9} \\ x &= \frac{9.8 \times 10^{-9}}{(0.10)^2} \\ &= 9.8 \times 10^{-7}\ M \end{aligned}$$

Thus, the molar solubility of PbI_2 in 0.10 M NaI solution is calculated to be 9.8×10^{-7} M.

We should always check to see if our simplifying assumption is valid. Notice that $2x$, which equals 2.0×10^{-6}, is indeed vastly smaller than 0.10, just as we anticipated. (If we add 2.0×10^{-6} to 0.10 and round correctly, we obtain 0.10.)

Is the Answer Reasonable? First, we can check the entries in the concentration table. The initial concentrations come from the solvent, which contains no Pb^{2+} but does contain 0.10 M I^-. By letting x equal the molar solubility, the coefficients of x in the "change" row equal the coefficients in the balanced equation for the equilibrium. At this point, we have checked the concentration table. To check the answer, we can recalculate the K_{sp}.

Practice Exercises

18.8 | Calculate the molar solubility of AgI in a 0.20 M CaI_2 solution. Compare the answer to the calculated molar solubility of AgI in pure water. (*Hint*: What is the I^- concentration in 0.20 M CaI_2?)

18.9 | Calculate the molar solubility of $Fe(OH)_3$ in a solution where the OH^- concentration is initially 0.050 M. Assume the dissociation of $Fe(OH)_3$ is 100%.

READ THESE TWO PARAGRAPHS!

A Mistake to Avoid

The most common mistake that students make with problems like Example 18.5 is to use the coefficient of an ion in the solubility equilibrium at the wrong moment in the calculation. The coefficient of I^- in the PbI_2 equilibrium is 2. The mistake is to use this 2 to double the *initial* concentration of I^-; however, the *initial* concentration of I^- was provided not by PbI_2 but by NaI. When 0.10 mol of NaI dissociates, it gives 0.10 mol of I^-, not 2 × 0.10 mol. *The coefficients in the equation for the equilibrium are only used to obtain the quantities in the "change" row.*

To avoid mistakes, it is useful to always view the formation of the final solution as a two-step process. You begin with a solvent into which the "insoluble solid" will be placed. In some problems, the solvent may be pure water, in which case the initial concentrations of the ions will be zero—see Examples 18.1–18.4. In other problems,

> like Example 18.5, the solvent will be a *solution* that contains a common ion. When this is so, first decide what the concentration of the common ion is and enter this value into the "initial concentration" row of the table. Next, imagine that the solid is added to the solvent and a little of it dissolves. *The amount that dissolves is what gives the values in the "change" row.* These entries must be in the same ratio as the coefficients in the equilibrium, which is accomplished if we let x be the molar solubility of the salt. Then, the coefficients of x will be the same as the coefficients of the ions in the balanced chemical equation for the equilibrium.

In Example 18.4, we found that the molar solubility of PbI_2 in *pure* water was 1.3×10^{-3} M. In water that contains 0.10 M NaI (Example 18.5), the solubility of PbI_2 is 9.8×10^{-7} M, well over a thousand times smaller. As we said, the common ion effect often causes huge reductions in the solubilities of sparingly soluble compounds by shifting the equilibrium toward the formation of the solid.

Determining whether a Precipitate Will Form

If we know the anticipated concentrations of the ions of a salt in a solution, we can use the value of K_{sp} for the salt to predict whether or not a precipitate should form. This is because the computed value for Q (the ion product) can tell us whether a solution is unsaturated, saturated, or supersaturated. *For a precipitate of a salt to form, the solution must be supersaturated.*

If the solution is unsaturated, its ion concentrations are less than required for saturation, Q is less than K_{sp}, and no precipitate will form. For a saturated solution, we have Q equal to K_{sp}, and no precipitate will form. (If a precipitate were to form, the solution would become unsaturated and the precipitate would redissolve.) If the solution is supersaturated, the ion concentrations exceed those required for saturation and Q is larger than K_{sp}. Only in this last instance should we expect a precipitate to form so that Q will be reduced to the value of the K_{sp}. This can be summarized as follows:

Precipitate will form	$Q > K_{sp}$	(supersaturated)
No precipitate will form	$Q = K_{sp}$	(saturated)
	$Q < K_{sp}$	(unsaturated)

TOOLS

Predicting precipitation

Let's look at some sample calculations.

Example 18.6

Predicting whether a Precipitate Will Form

Suppose we want to prepare 0.500 L of a solution containing 0.0075 mol of NaCl and 0.075 mol of $Pb(NO_3)_2$. Knowing from the solubility rules that the chloride of Pb^{2+} is "insoluble," we are concerned that a precipitate of $PbCl_2$ might form. Will it?

■ **Analysis:** To find out whether a precipitate will form, we will have to compare the value of Q, computed using the data in the problem, with K_{sp}. Then, we can apply the criteria above. This also means that we have to write the correct ion product expression and we're going to have to calculate the molar concentrations of the Pb^{2+} and Cl^- ions in the solution.

■ **Assembling the Tools:** To calculate the value of Q, our tool is the appropriate ion product for $PbCl_2$, which we can obtain by writing the solubility equilibrium equation and the K_{sp} expression that applies to a saturated solution of $PbCl_2$:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = [Pb^{2+}][Cl^-]^2$$

From Table 18.1, $K_{sp} = 1.7 \times 10^{-5}$.

We also have to compute the molar concentrations of the ions. The definition of molarity provides the necessary tool, by taking the ratio of moles to volume (in liters):

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Solution: The planned solution would have the following molar concentrations:

$$[\mathrm{Pb}^{2+}] = \frac{0.075\ \mathrm{mol}}{0.500\ \mathrm{L}} = 0.15\ M \qquad [\mathrm{Cl}^-] = \frac{0.0075\ \mathrm{mol}}{0.500\ \mathrm{L}} = 0.015\ M$$

It is usually difficult to prevent the extra salt from precipitating out of a supersaturated solution. (Sodium acetate is a notable exception. Supersaturated solutions of this salt are easily made.)

We use these values to compute the ion product for $PbCl_2$ in the solution:

$$Q = [\mathrm{Pb}^{2+}][\mathrm{Cl}^-]^2 = (0.15)(0.015)^2 = 3.4 \times 10^{-5}$$

This value of Q is larger than the K_{sp} of $PbCl_2$, 1.7×10^{-5}, which means that a precipitate of $PbCl_2$ will form if we attempt to prepare this solution.

Is the Answer Reasonable? We can double-check that the molarities of the ions in the planned solution are correct. Then we check the calculation of Q. All seems to be in order, so we have confidence that our answer is correct.

Practice Exercises

18.10 | Calculate the ion product for the solution in which the Ca^{2+} concentration is 0.0025 M and the SO_4^{2-} concentration is 0.030 M. Will a precipitate of $CaSO_4$ form in this solution? (*Hint*: What is the form of the ion product for $CaSO_4$?)

18.11 | Calculate the ion product for a solution containing $3.4 \times 10^{-4}\ M$ CrO_4^{2-} and $4.8 \times 10^{-5}\ M$ Ag^+. Will a precipitate form?

Example 18.7
Predicting whether a Precipitate Will Form

What possible precipitate might form by mixing 50.0 mL of $1.0 \times 10^{-4}\ M$ NaCl with 50.0 mL of $1.0 \times 10^{-6}\ M$ $AgNO_3$? Will it form? (Assume the volumes are additive.)

Analysis: In this problem we are being asked, in effect, whether a metathesis reaction will occur between NaCl and $AgNO_3$. We should be able to use the solubility rules in Chapter 5 to predict whether this *might* occur. If the solubility rules suggest a precipitate, we can then calculate the ion product for the compound using the concentrations of the ions in the final solution. If this ion product exceeds K_{sp} for the salt, then a precipitate is expected.

To calculate Q correctly requires that we use the concentrations of the ions *after the solutions have been mixed*. Therefore, before computing the ion product, we must first take into account that mixing the solutions dilutes each of the solutes. Dilution problems were covered in Chapter 5.

To obtain the solution to this problem we must bring together tools from two different chapters.

Assembling the Tools: Our first tool is the solubility rules (page 176), which helps us determine whether each product is soluble or insoluble. Then, we need to use the dilution equation from Chapter 5, Equation 5.6 (page 189), to find the concentrations of the ions for the ion product. Finally, we will use the ion product and compare Q to K_{sp} to determine if a precipitate forms.

■ **Solution:** Let's begin by writing the equation for the potential metathesis reaction between NaCl and $AgNO_3$. The solubility rules (page 176) help us determine whether each product is soluble or insoluble.

$$\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$$

The solubility rules indicate that we expect a precipitate of AgCl. But are the concentrations of Ag^+ and Cl^- actually high enough?

In the original solutions, the 1.0×10^{-6} *M* $AgNO_3$ contains 1.0×10^{-6} *M* Ag^+ and the 1.0×10^{-4} *M* NaCl contains 1.0×10^{-4} *M* Cl^-. What are the concentrations of these ions after dilution? To determine these, we use Equation 5.6, which applies to all dilution problems involving molarity:

$$V_{\mathrm{dil}} \cdot M_{\mathrm{dil}} = V_{\mathrm{conc}} \cdot M_{\mathrm{conc}}$$

Solving for M_{dil} gives

$$M_{\mathrm{dil}} = \frac{M_{\mathrm{conc}} V_{\mathrm{conc}}}{V_{\mathrm{dil}}}$$

The initial volumes of the more concentrated solutions are 50.0 mL, and when the two solutions are combined, the final total volume is 100.0 mL. Therefore,

$$[\mathrm{Ag^+}]_{final} = \frac{(50.0\ \mathrm{mL})(1.0 \times 10^{-6}\ M)}{100.0\ \mathrm{mL}} = 5.0 \times 10^{-7}\ M$$

$$[\mathrm{Cl^-}]_{final} = \frac{(50.0\ \mathrm{mL})(1.0 \times 10^{-4}\ M)}{100.0\ \mathrm{mL}} = 5.0 \times 10^{-5}\ M$$

Now we use these to calculate *Q* for AgCl, which we can obtain from the dissociation reaction of the salt:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

$$Q = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

Substituting the concentrations computed above gives

$$Q = (5.0 \times 10^{-7})(5.0 \times 10^{-5}) = 2.5 \times 10^{-11}$$

In Table 18.1, the K_{sp} for AgCl is given as 1.8×10^{10}. Notice that *Q* is *smaller* than K_{sp}, which means that the final solution is unsaturated in AgCl and a precipitate will *not* form.

■ **Is the Answer Reasonable?** There are several things we should check here. They include writing the equation for the metathesis reaction, calculating the concentrations of the ions after dilution (we've doubled the volume, so the concentrations are halved), and setting up the correct ion product. All appear to be correct, so the answer should be okay.

Practice Exercises

18.12 | What precipitate might be expected if we mix 100.0 mL of 1.0×10^{-3} *M* $Pb(NO_3)_2$ and 100.0 mL of 2.0×10^{-3} *M* $MgSO_4$? Will some precipitate form? Assume that the volumes are additive. (*Hint*: What tools will you need to solve the problem?)

18.13 | What precipitate might be expected if we mix 50.0 mL of 0.10 *M* $Pb(NO_3)_2$ and 20.0 mL of 0.040 *M* NaCl? Will some precipitate form? Assume that the volumes are additive.

Analyzing and Solving Multi-Concept Problems

A saturated solution of $PbCl_2$ has a freezing point of −0.089 °C. What is the K_{sp} of $PbCl_2$ as determined by the freezing point depression value? Assume that lead(II) chloride dissociates completely and that the density of the solution is 1.00 g mL^{-1}.

Analysis In this question we are asked to find the K_{sp} for the $PbCl_2$. In order to do this, we need to find the concentration of the $PbCl_2$. We are given the freezing point depression for the solution, so we can use this to determine the concentration of the solute.

PART 1

Assembling the Tools The first tool we will need is the freezing point depression equation,

$$\Delta T_f = K_f m$$

Solution Let us rearrange the equation to find the molality of the solution

$$\Delta T_f = K_f m$$
$$m = \frac{\Delta T_f}{K_f}$$

We have the ΔT_f, which equals 0.089 °C, and from Table 13.3 (page 609), $K_f = 1.86\ °C\ m^{-1}$. Substituting these values into the equation gives us

$$m = \frac{0.089\ \cancel{°C}}{1.86\ \cancel{°C}\ m^{-1}}$$
$$m = 0.048\ m$$

Now this gives us the molality of all of the ions in the solution, but we need the molarity, so we also need to convert between molality (moles of solute per kilogram of solvent) and molarity (moles of solute per liter of solution). We are given the density of the solution as 1.00 g mL^{-1}.

$$M = \frac{0.048 \text{ mol solute}}{\cancel{1 \text{ kg of water}}} \times \frac{\cancel{1 \text{ kg water}}}{1000\ \cancel{\text{g water}}} \times \frac{1.00\ \cancel{\text{g water}}}{1.00\ \cancel{\text{mL solution}}} \times \frac{1000\ \cancel{\text{mL solution}}}{1 \text{ L solution}}$$
$$M = 0.048 \text{ mol L}^{-1}$$

PART 2

Assembling the Tools Now that we have the molarity of the ions in the solution, we need to determine the K_{sp}. We now use the molarity of the ions, the chemical equation, and its solubility product expression to solve the problem.

Solution Before we start substituting numbers into the solubility product expression, we have to think about what happened to bring the ions into solution. The $PbCl_2$ dissolved, the ions dissociated, and for each $PbCl_2$ formula unit that dissolved, one Pb^{2+} and two Cl^- went into solution. So if x moles of $PbCl_2$ dissolved, then x mole of Pb^{2+} and $2x$ moles of Cl^- are in solution. The volume of the solution is the same for lead and chloride, so we can add the molarities instead of the moles. To calculate the actual concentration of each ion in solution we have

$$0.048\ M \text{ ions} = x\ M\ Pb^{2+} + 2x\ M\ Cl^-$$
$$0.048\ M \text{ ions} = 3x\ M$$
$$x = 0.016\ M$$
$$[Pb^{2+}] = 0.016\ M \quad \text{and} \quad [Cl^-] = 0.032\ M$$

Now we can substitute these values into the expression for K_{sp}.

$$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^-$$
$$K_{sp} = [Pb^{2+}][Cl^-]^2$$
$$K_{sp} = [0.016][0.032]^2$$
$$K_{sp} = 1.6 \times 10^{-5}$$

■ **Are the Answers Reasonable?** The freezing point depression is relatively small, so we do not expect to have very much solute dissolved, and from our calculations, this is correct. Next, we have calculated a K_{sp} value that is very similar to the value in Table 18.1, so this is also an indication that our calculation is correct. Finally, we realized that the total ion concentration comes from the dissociation of the ions, so the concentration of each ion is a fraction of the total ion concentration.

■ The low solubility of the salt indicates that our assumption about completely dissociated ions is reasonable.

18.2 | Equilibria in Solutions of Metal Oxides and Sulfides

Aqueous equilibria involving insoluble oxides and sulfides are more complex than those we've considered so far because of reactions of the anions with the solvent, water.

When a metal oxide dissolves in water, it does so by reacting with water instead of by a simple dissociation of ions that remain otherwise unchanged. Sodium oxide, for example, consists of Na^+ and O^{2-} ions, and it readily dissolves in water. The solution, however, does not contain the oxide ion, O^{2-}. Instead, the hydroxide ion forms. The equation for the reaction is

$$Na_2O(s) + H_2O \longrightarrow 2NaOH(aq)$$

This actually involves the reaction of oxide ions with water as the crystals of Na_2O break up:

$$O^{2-}(s) + H_2O \longrightarrow 2OH^-(aq)$$

The oxide ion is simply too powerful a base to exist in water at any concentration worthy of experimental note. We can understand why from the extraordinarily high (estimated) value of K_b for O^{2-}, 1×10^{22}. Thus, there is no way to supply *oxide ions* to an aqueous solution in order to form an insoluble metal oxide directly. Oxide ions react with water, instead, to generate the hydroxide ion. When an insoluble metal *oxide* instead of an insoluble metal *hydroxide* does precipitate from a solution, it forms because the specific metal ion is able to react with OH^-, extract O^{2-}, and leave H^+ (or H_2O) in the solution. The silver ion, for example, precipitates as brown silver oxide, Ag_2O, when OH^- is added to aqueous silver salts (Figure 18.3):

$$2Ag^+(aq) + 2OH^-(aq) \longrightarrow Ag_2O(s) + H_2O$$

The reverse of this reaction, written as an equilibrium, corresponds to the solubility equilibrium for Ag_2O:

$$Ag_2O(s) + H_2O \rightleftharpoons 2Ag^+(aq) + 2OH^-(aq)$$

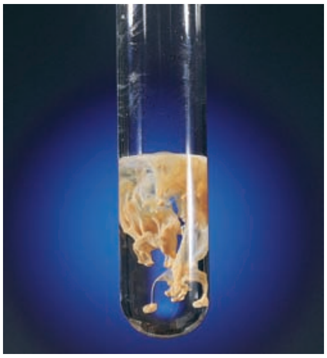

Figure 18.3 | **Silver oxide.** A brown, mud-like precipitate of silver oxide forms as a sodium hydroxide solution is added to a solution of silver nitrate. *(Michael Watson)*

Solubility Equilibria for Metal Sulfides and Oxides

When we shift from oxygen to sulfur in Group 6A and consider metal sulfides, we find many similarities to oxides. One is that the sulfide ion, S^{2-}, like the oxide ion, O^{2-}, is such a strong Brønsted–Lowry base that it does not exist in any ordinary aqueous solution.

The sulfide ion has not been detected in an aqueous solution, even in the presence of 8 *M* NaOH, where one might think that the reaction

$$OH^- + HS^- \longrightarrow H_2O + S^{2-}$$

could generate some detectable S^{2-}. An 8 *M* NaOH solution is at a concentration well outside the bounds of the "ordinary." Thus, Na_2S, like Na_2O, dissolves in water *by reacting with it,* not by releasing an otherwise unchanged divalent anion, S^{2-}:

$$Na_2S(s) + H_2O \longrightarrow 2Na^+(aq) + HS^-(aq) + OH^-(aq)$$

As with Na_2O, water reacts with the sulfide ion as the crystals break apart and the ions enter the solution:

$$S^{2-}(s) + H_2O \longrightarrow HS^-(aq) + OH^-(aq)$$

■ In the laboratory, the qualitative analysis of metal ions uses the precipitation of metal sulfides to separate some metal ions from others.

The sulfides of most metals have quite low solubilities in water. Simply bubbling hydrogen sulfide gas into an aqueous solution of any one of a number of metal ions—Cu^{2+}, Pb^{2+}, and Ni^{2+}, for example—causes their sulfides to precipitate. Many of these have distinctive colors (Figure 18.4) that can be used to help identify which metal ion is in solution.

To write the solubility equilibrium for an insoluble metal sulfide, we have to take into account the reaction of the sulfide ion with water. For example, for CuS the equilibrium is best written as

$$CuS(s) + H_2O \rightleftharpoons Cu^{2+}(aq) + HS^-(aq) + OH^-(aq) \qquad \textbf{(18.2)}$$

This equation yields the ion product $[Cu^{2+}][HS^-][OH^-]$, and the solubility product constant for CuS is expressed by the equation,

$$K_{sp} = [Cu^{2+}][HS^-][OH^-]$$

Values of K_{sp} of this form for a number of metal sulfides are listed in the last column in Table 18.2. Notice particularly how much the K_{sp} values vary—from 2×10^{-53} to 3×10^{-11}, a spread of a factor of 10^{42}.

Acid-Insoluble Sulfides

Many metal sulfides are able to react with acid and thereby dissolve. An example is zinc sulfide:

$$ZnS(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2S$$

However, some metal sulfides, referred to as the *acid-insoluble sulfides,* have K_{sp} values so low that they do not dissolve in acid. The cations in this group can be precipitated from the other cations simply by bubbling hydrogen sulfide into a sufficiently acidic solution that contains several metal ions.

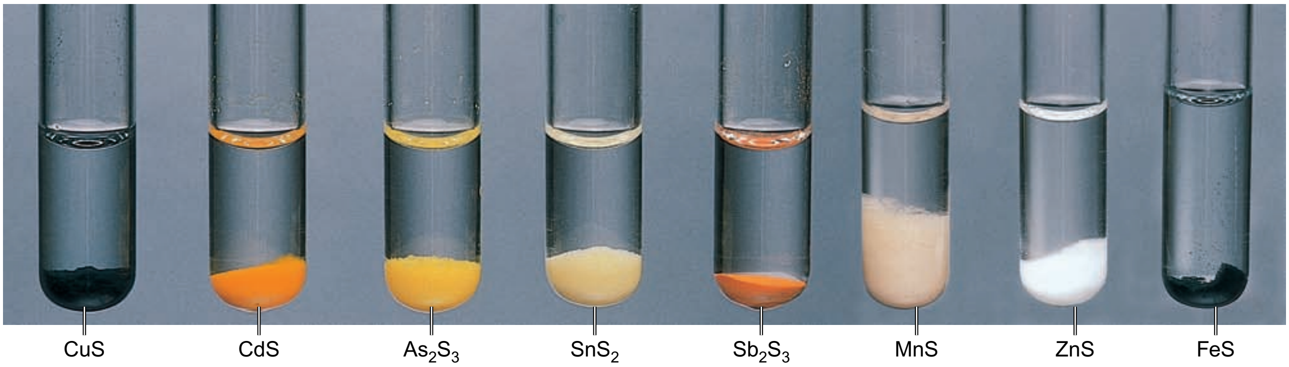

Figure 18.4 | **The colors of some metal sulfides.** *(OPC, Inc.)*

Table 18.2 Metal Ions Separable by Selective Precipitation of Sulfides[a]

Metal Ion	Sulfide	K_{spa}	K_{sp}
Acid-Insoluble Sulfides			
Hg^{2+}	HgS (black form)	2×10^{-32}	2×10^{-53}
Ag^{+}	Ag_2S	6×10^{-30}	6×10^{-51}
Cu^{2+}	CuS	6×10^{-16}	6×10^{-37}
Cd^{2+}	CdS	8×10^{-7}	8×10^{-28}
Pb^{2+}	PbS	3×10^{-7}	3×10^{-28}
Sn^{2+}	SnS	1×10^{-5}	1×10^{-26}
Base-Insoluble Sulfides (Acid-Soluble Sulfides)			
Zn^{2+}	α–ZnS	2×10^{-4}	2×10^{-25}
	β–ZnS	3×10^{-2}	3×10^{-23}
Co^{2+}	CoS	5×10^{-1}	5×10^{-22}
Ni^{2+}	NiS	4×10^{1}	4×10^{-20}
Fe^{2+}	FeS	6×10^{2}	6×10^{-19}
Mn^{2+}	MnS (pink form)	3×10^{10}	3×10^{-11}
	MnS (green form)	3×10^{7}	3×10^{-14}

[a] Data are for 25 °C. See R. J. Meyers, *J. Chem. Ed.*, vol. 63, 1986, p. 687.

When the solution is acidic, we have to treat the solubility equilibria differently. In acid, HS^- and OH^- would be neutralized, leaving their conjugate acids, H_2S and H_2O. Under these conditions, the equation for the solubility equilibrium becomes

$$CuS(s) + 2H^+(aq) \rightleftharpoons Cu^{2+}(aq) + H_2S(aq)$$

This changes the mass action expression for the solubility product equilibrium, which we will now call the **acid solubility product, K_{spa}**. The *a* in the subscript indicates that the medium is acidic.

$$K_{spa} = \frac{[Cu^{2+}][H_2S]}{[H^+]^2}$$

TOOLS

Acid solubility product constant, K_{spa}

Table 18.2 also lists K_{spa} values for the metal sulfides. Notice that all K_{spa} values are about 10^{21} larger than the K_{sp} values. Metal sulfides are clearly vastly more soluble in dilute acid than in water. Yet several—the acid-insoluble sulfides—are so insoluble that even the most soluble of them, SnS, barely dissolves, even in moderately concentrated acid. So, there are two families of sulfides, the *acid-insoluble sulfides* and the acid-soluble ones, otherwise known as the *base-insoluble sulfides*. As we discuss in Section 18.3, the differing solubilities of their sulfides in acid provide a means of separating the two classes of metal ions from each other.

18.3 | Selective Precipitation

Selective precipitation means causing one metal ion to precipitate while holding another in solution. Often this is possible because of large differences in the solubilities of salts that we would generally consider to be insoluble. For example, the K_{sp} values for AgCl and $PbCl_2$ are 1.8×10^{-10} and 1.7×10^{-5}, respectively, which gives them molar solubilities in water of 1.3×10^{-5} *M* for AgCl and 1.6×10^{-2} *M* for $PbCl_2$. In terms of molar solubilities, lead(II) chloride is approximately 1200 times more soluble in water than AgCl. If we had a solution containing both 0.10 *M* Pb^{2+} and 0.10 *M* Ag^+ and began adding Cl^-, AgCl would precipitate first (Figure 18.5). In fact, we can calculate that before any $PbCl_2$

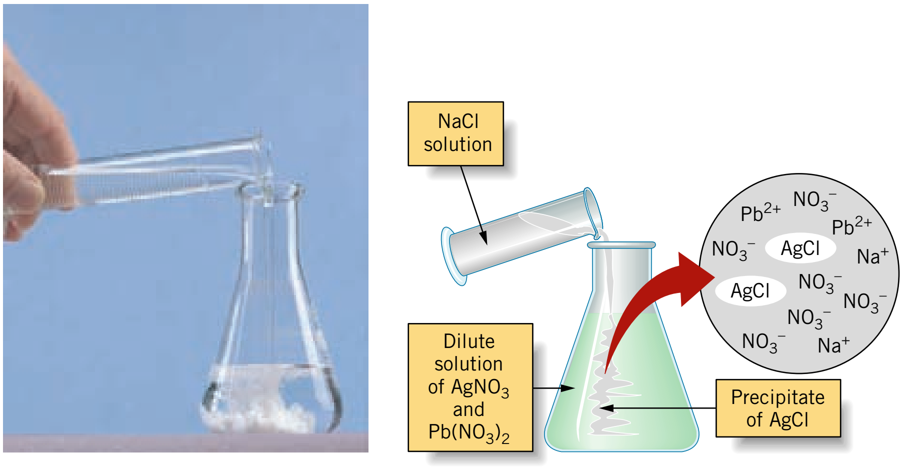

Figure 18.5 | **Selective precipitation.** When dilute sodium chloride is added to a solution containing both Ag^+ ions and Pb^{2+} ions (both dissolved as their nitrate salts), the less soluble AgCl precipitates before the more soluble $PbCl_2$. Precipitation of the AgCl is nearly complete before any $PbCl_2$ begins to form. *(Andy Washnik)*

starts to precipitate, the concentration of Ag^+ will have been reduced to 1.6×10^{-8} *M*. Thus, nearly all of the silver is removed from the solution without precipitating any of the lead, and the ions are effectively separated. All we need to do is find a way of adjusting the concentration of the Cl^- to achieve the separation.

Example 18.8
Selective Precipitation of Silver Halides

If a solution contains 0.10 *M* Cl^- and 0.10 *M* I^-, then what concentration of $AgNO_3$ will allow the separation of these halides by selective precipitation?

■ **Analysis:** We are being asked to find the concentration of Ag^+ ions that will remove one of the ions from the solution while leaving the other behind. We will have to decide which solid will precipitate first, and then determine the concentration of the silver ions that will precipitate the first solid and leave the second solid dissolved in the solution.

■ **Assembling the Tools:** From Table 18.1, we can find the ion product constants

$$\begin{aligned} \mathrm{AgCl}(s) &\rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \qquad K_{sp} = 1.8 \times 10^{-10} \\ \mathrm{AgI}(s) &\rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{I^-}(aq) \qquad K_{sp} = 8.5 \times 10^{-17} \end{aligned}$$

Silver iodide is much less soluble than silver chloride, so silver iodide will precipitate first, and the silver iodide solid can be filtered off to leave the chloride ions in solution.

Next, we have to determine the concentration of the silver ions that will precipitate the iodide. To do this, we can imagine that we start with no silver in solution, and that we slowly add the silver ions. As we increase the concentration of the silver, the iodide precipitates; this is the lowest concentration of silver that needs to be added. Then, we add more silver, and more iodide precipitates, until at a certain concentration, the solution becomes saturated in AgCl. This is the maximum concentration of Ag^+ that we can have without causing AgCl to precipitate. This is what we need to calculate.

■ **Solution:** We can start by determining what concentration of Ag^+ will precipitate AgCl. We know that the concentration of Cl^- is 0.10 *M*, so we can use the solubility product expression to solve for the concentration of Ag^+ required to produce saturation:

$$\begin{aligned} \mathrm{AgCl}(s) &\rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \\ K_{sp} &= [\mathrm{Ag^+}][\mathrm{Cl^-}] \\ 1.8 \times 10^{-10} &= [\mathrm{Ag^+}](0.10\ M) \\ 1.8 \times 10^{-9}\ M &= [\mathrm{Ag^+}] \end{aligned}$$

As long as the concentration of the silver ion is kept at or below $1.8 \times 10^{-9}\ M$, then the chloride ion will *not* precipitate. Now the question is, will the I^- concentration be reduced enough to consider the ions to be effectively separated?

Let's use the concentration of silver ions to calculate how much iodide will be in solution:

$$\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{I}^-(aq)$$

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{I}^-]$$

$$8.5 \times 10^{-17} = (1.8 \times 10^{-9}\ M)[\mathrm{I}^-]$$

$$4.7 \times 10^{-8}\ M = [\mathrm{I}^-]$$

The iodide was 0.10 M before the addition of the silver ions, and now it is $4.7 \times 10^{-8}\ M$. We can consider the iodide completely precipitated. So the maximum concentration of silver ion needed to achieve effective separation is $1.8 \times 10^{-9}\ M$.

■ **Is the Answer Reasonable?** From our work we showed that the silver iodide precipitated well before the silver chloride. Considering the differences in the K_{sp} values, this is to be expected. We can go back and check the math, and make sure that our reasoning was correct.

Practice Exercises

18.14 | If a solution contains calcium ions (0.25 M) and barium ions (0.05 M), what concentration of SO_4^{2-} would be required to selectively precipitate the barium ions from solution? (*Hint*: First find the concentration of sulfate ions that will cause the calcium ions to precipitate.)

18.15 | A solution contains 0.20 M $CaCl_2$ and 0.10 M $MgCl_2$. What concentration of hydroxide ions would be required to separate the magnesium as $Mg(OH)_2$ without precipitating the calcium as $Ca(OH)_2$?

Metal Sulfides

The large differences in K_{spa} values between the acid-insoluble and the base-insoluble metal sulfides make it possible to separate the corresponding cations from each other by adjusting the pH of the solution. The sulfides of the acid-insoluble cations are selectively precipitated by hydrogen sulfide from a solution by adjusting the pH so that the other cations remain in solution. A solution saturated in H_2S is used, for which the molarity of H_2S is 0.1 M.

Example 18.9 shows how we can calculate the pH needed to selectively precipitate two metal cations as their sulfides. We will use Cu^{2+} and Ni^{2+} ions to represent a cation from each class.

Example 18.9

Selective Precipitation of the Sulfides of Acid-Insoluble Cations from Base-Insoluble Cations

Over what range of hydrogen ion concentrations (and pH) is it possible to separate Cu^{2+} from Ni^{2+} when both metal ions are present in a solution at a concentration of 0.010 M and the solution is made saturated in H_2S (where $[H_2S] = 0.1\ M$)?

■ **Analysis:** Both the concentration of the H_2S and the Cu^{2+} and Ni^{2+} ions are known, so we are only changing the concentration of the hydrogen ion, and we are being asked for a range of hydrogen ion concentrations. The low end of the hydrogen ion concentration will be the more basic solution, and the high end will be the more acidic solution. Sulfides become more soluble as the hydrogen ion concentration increases.

The problem reduces to two questions. The first question is: What is the most basic solution that will keep the more soluble sulfide in solution? The answer to this will be the *lower limit* on $[H^+]$. At any lower H^+ concentration, this compound will precipitate, so we want an H^+ concentration equal to or greater than this value. The second question is: What hydrogen ion concentration would be needed to keep the less soluble sulfide *in solution*? (The answer to this question will give us the *upper limit* on $[H^+]$; we would really want a lower H^+ concentration, so the less soluble sulfide *will* precipitate.) Once we know these limits, we know that any hydrogen ion concentration in between them will permit the less soluble sulfide to precipitate but retain the more soluble sulfide in solution.

■ **Assembling the Tools:** We need the appropriate equilibrium expressions and the K_{spa} values from Table 18.2, from which we can write the equilibrium laws needed to work the problem:

$$\mathrm{CuS}(s) + 2\mathrm{H}^+(aq) \rightleftharpoons \mathrm{Cu}^{2+}(aq) + \mathrm{H_2S}(aq) \qquad K_{spa} = \frac{[\mathrm{Cu}^{2+}][\mathrm{H_2S}]}{[\mathrm{H}^+]^2} = 6 \times 10^{-16}$$

$$\mathrm{NiS}(s) + 2\mathrm{H}^+(aq) \rightleftharpoons \mathrm{Ni}^{2+}(aq) + \mathrm{H_2S}(aq) \qquad K_{spa} = \frac{[\mathrm{Ni}^{2+}][\mathrm{H_2S}]}{[\mathrm{H}^+]^2} = 4 \times 10^{1}$$

NiS is much more soluble in an acidic solution than CuS. As the concentration of H^+ increases, the more soluble the NiS will be. (Actually, both will become more soluble, but NiS is much more soluble than CuS.) Therefore, we need an H^+ concentration that will be large enough to prevent NiS from precipitating, but small enough so that CuS does precipitate. We will use the equilibrium constant expressions to calculate the H^+ concentrations for the limits of the solubility of CuS and NiS.

■ **Solution:** We will obtain the lower limit first, by calculating the $[H^+]$ required based on a concentration of Ni^{2+} equal to 0.010 *M* and an H_2S concentration of 0.1 *M*. If we keep the value of $[H^+]$ *equal to or larger* than this value, then NiS will be prevented from precipitating. First, we substitute values into the K_{spa} expression:

$$K_{spa} = \frac{[\mathrm{Ni}^{2+}][\mathrm{H_2S}]}{[\mathrm{H}^+]^2} = \frac{(0.010)(0.1)}{[\mathrm{H}^+]^2} = 4 \times 10^{1}$$

Now we solve for $[H^+]$:

$$[\mathrm{H}^+]^2 = \frac{(0.010)(0.1)}{4 \times 10^{1}}$$

$$[\mathrm{H}^+] = 5 \times 10^{-3}\ M$$

At any $[H^+]$ lower than this, the $[H^+]$ will not be great enough to keep the NiS in solution. This is a pH of 2.3.

Next, we will find the upper limit. If CuS *does not precipitate*, the Cu^{2+} concentration will be the given value, 0.010 *M*, so we substitute this along with the H_2S concentration (0.1 *M*) into the expression for K_{spa} of Cu^{2+}:

$$K_{spa} = \frac{[\mathrm{Cu}^{2+}][\mathrm{H_2S}]}{[\mathrm{H}^+]^2} = \frac{(0.010)(0.1)}{[\mathrm{H}^+]^2} = 6 \times 10^{-16}$$

Now we solve for $[H^+]$:

$$[\mathrm{H}^+]^2 = \frac{(0.010)(0.1)}{6 \times 10^{-16}} = 2 \times 10^{12}$$

$$[\mathrm{H}^+] = 1 \times 10^{6}\ M$$

If we could make $[H^+] = 1 \times 10^6$ *M*, we could prevent CuS from forming. However, it isn't possible to have 10^6 or a *million* moles of H^+ per liter! What the calculated $[H^+]$ tells us, therefore, is that *no matter how acidic the solution is, we cannot prevent* CuS *from precipitating when we saturate the solution with* H_2S. (You can now see why CuS is classed as an "acid-insoluble sulfide.")

Now, we have our limits: the lower limit for the concentration of H^+ is $5 \times 10^{-3}\ M$ and there is no actual higher limit, since the theoretical higher limit is beyond any possible physical means.

If we maintain the pH of the solution of 0.010 M Cu^{2+} and 0.010 M Ni^{2+} at 2.3 or lower (more acidic), as we make the solution saturated in H_2S, then virtually all of the Cu^{2+} will precipitate as CuS, but all of the Ni^{2+} will remain in solution.

■ **Is the Answer Reasonable?** The K_{spa} values certainly tell us that CuS is quite insoluble in acid and that NiS is a lot more soluble, so from that standpoint the results seem reasonable. There's not much more we can do to check the answer, other than to review the entire set of calculations.

Practice Exercises

18.16 | Suppose a solution contains 0.0050 M Co^{2+} and is saturated with H_2S (with $[H_2S] = 0.1\ M$). Would CoS precipitate if the solution has a pH of 3.5? (*Hint*: What relationship do we use to determine whether a precipitate is going to form in a solution?)

18.17 | Consider a solution containing Hg^{2+} and Fe^{2+}, both at molarities of 0.010 M. It is to be saturated with H_2S. Calculate the highest pH that this solution could have that would keep Fe^{2+} in solution while causing Hg^{2+} to precipitate as HgS.

In actual lab work, separation of the acid-insoluble sulfides from the base-insoluble ones is performed with $[H^+] \approx 0.3\ M$, which corresponds to a pH of about 0.5. This ensures that the base-insoluble sulfides will not precipitate. The calculation in Example 18.9 also demonstrated why NiS can be classified as a "base-insoluble sulfide." If the solution is *basic* when it is made saturated in H_2S, the pH will surely be larger than 2.3 and NiS will precipitate.

Metal Carbonates

The principles of selective precipitation by the control of pH apply to any system where the anion is that of a weak acid. The metal carbonates can also be selectively precipitated, with many being quite insoluble in water (see Table 18.1). The dissociation of magnesium carbonate in water, for example, involves the following equilibrium and K_{sp} equations:

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3{}^{2-}(aq) \qquad K_{sp} = 6.8 \times 10^{-8}$$

For strontium carbonate, the equations are

$$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3{}^{2-}(aq) \qquad K_{sp} = 5.6 \times 10^{-10}$$

Would it be possible to separate the magnesium ion from the strontium ion by taking advantage of the difference in K_{sp} of their carbonates?

We can do so if we can control the carbonate ion concentration. Because the carbonate ion is a relatively strong Brønsted–Lowry base, its control is available, indirectly, by adjusting the pH of the solution. This is because the hydrogen ion is one of the species in each of the following equilibria.[3]

$$\begin{aligned} H_2CO_3(aq) &\rightleftharpoons H^+(aq) + HCO_3{}^-(aq) \qquad K_{a_1} = 4.3 \times 10^{-7} \\ HCO_3{}^-(aq) &\rightleftharpoons H^+(aq) + CO_3{}^{2-}(aq) \qquad K_{a_2} = 5.6 \times 10^{-11} \end{aligned}$$

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[3] The situation involving aqueous carbonic acid is complicated by the presence of dissolved CO_2, which we could represent in an equation as $CO_2(aq)$. In fact, this is how most of the dissolved CO_2 exists—namely, as $CO_2(aq)$, not as $H_2CO_3(aq)$. However, we may use $H_2CO_3(aq)$ as a surrogate or stand-in for $CO_2(aq)$, because the latter changes smoothly to the former on demand. The following two successive equilibria involving carbonic acid exist in a solution of aqueous CO_2:

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3{}^-(aq)$$

The value of K_{a_1} cited here for $H_2CO_3(aq)$ is really the product of the equilibrium constants of these two equilibria.

You can see that if we increase the hydrogen ion concentration, both equilibria will shift to the left, in accordance with Le Châtelier's principle, and this will reduce the concentration of the carbonate ion. The value of $[CO_3^{2-}]$ thus decreases with decreasing pH. On the other hand, if we decrease the hydrogen ion concentration, making the solution more basic, we will cause the two equilibria to shift to the right. The concentration of the carbonate ion thus increases with increasing pH.

For the calculations ahead, it will be useful to combine the two hydrogen carbonate equilibria into one overall equation that relates the molar concentrations of carbonic acid, carbonate ion, and hydrogen ion. So, we first add the two:

$$\begin{array}{r@{\;}l}
H_2CO_3(aq) & \rightleftharpoons H^+(aq) + HCO_3^-(aq) \\
HCO_3^-(aq) & \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \\
\hline
H_2CO_3(aq) & \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)
\end{array} \qquad \textbf{(18.3)}$$

Recall from Chapter 15 that when we add two equilibria to get a third, the equilibrium constant of the latter is the product of those of the two equilibria that are combined. Thus, for Equation 18.3, the equilibrium constant, which we'll symbolize as K_a, is obtained as follows:

TOOLS

Combined K_a expression for a diprotic acid

$$K_a = K_{a_1} \times K_{a_2} = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} \qquad \textbf{(18.4)}$$

$$= (4.3 \times 10^{-7}) \times (5.6 \times 10^{-11})$$

$$= 2.4 \times 10^{-17}$$

■ We can safely use Equation 18.4 *only* when two of the three concentrations are known.

With this K_a value we may now study how to find the pH range within which Mg^{2+} and Sr^{2+} can be separated by taking advantage of their difference in K_{sp} values. To perform such a separation we would saturate a solution with CO_2, which provides H_2CO_3 through the rapidly established equilibrium,

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)$$

Thus, a solution that contains 0.030 M CO_2 has an effective H_2CO_3 concentration of 0.030 M.

Example 18.10

Separation of Metal Ions by the Selective Precipitation of Their Carbonates

A solution contains magnesium nitrate and strontium nitrate, each at a concentration of 0.10 M. Carbon dioxide is to be bubbled in to make the solution saturated in $CO_2(aq)$—approximately 0.030 M. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other?

■ **Analysis:** There are really two parts to this. First, what is the range in values of $[CO_3^{2-}]$ that allow one carbonate to precipitate but not the other? Second, given this range, what are the values of the solution's pH that produce this range in $[CO_3^{2-}]$ values?

To answer the first question, we will use the K_{sp} values of the two carbonate salts and their molar concentrations to find the CO_3^{2-} concentrations in their saturated solutions. To keep the more soluble carbonate from precipitating, the CO_3^{2-} concentration must be at or below that required for saturation. For the less soluble of the two, we must have a CO_3^{2-} concentration larger than in a saturated solution so that it will precipitate.

To answer the second question, we will use the combined K_a expression for H_2CO_3 to find the $[H^+]$ that gives the necessary CO_3^{2-} concentrations obtained in answering the first question. Having these $[H^+]$, it is then a simple matter to convert them to pH values.

■ **Assembling the Tools:** The tools we need to solve the problem are the K_{sp} values and equilibria for $MgCO_3$ and $SrCO_3$:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}] = 6.8 \times 10^{-8}$$
$$K_{sp} = [Sr^{2+}][CO_3^{2-}] = 5.6 \times 10^{-10}$$

We also need the combined K_a expression for carbonic acid:

$$K_a = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} = 2.4 \times 10^{-17}$$

■ **Solution:** Let's find the $[CO_3^{2-}]$ values required to give saturated solutions of these two salts.

For magnesium carbonate:

$$[CO_3^{2-}] = \frac{K_{sp}}{[Mg^{2+}]} = \frac{6.8 \times 10^{-8}}{0.10} = 6.8 \times 10^{-7}\ M$$

For strontium carbonate:

$$[CO_3^{2-}] = \frac{K_{sp}}{[Sr^{2+}]} = \frac{5.6 \times 10^{-10}}{0.10} = 5.6 \times 10^{-9}\ M$$

On the basis of the K_{sp} values, we see that $MgCO_3$ is the more soluble of the two. For separation, we have to keep the $[CO_3^{2-}]$ larger than 5.6×10^{-9} *M* and less than or equal to 6.8×10^{-7} *M* to keep the $MgCO_3$ in solution and to precipitate the $SrCO_3$.

$[CO_3^{2-}] > 5.6 \times 10^{-9}\ M$ (to precipitate $SrCO_3$)
$[CO_3^{2-}] \le 6.8 \times 10^{-7}\ M$ (to prevent $MgCO_3$ from precipitating)

The second phase of our calculation now asks what values of $[H^+]$ correspond to the calculated limits on $[CO_3^{2-}]$. For this we will use the K_a expression given by Equation 18.3. First, we solve for the square of $[H^+]$, using the molarity of the dissolved CO_2, 0.030 *M*, as the value of $[H_2CO_3]$. This gives us

$$[H^+]^2 = K_a \times \frac{[H_2CO_3]}{[CO_3^{2-}]}$$
$$[H^+]^2 = 2.4 \times 10^{-17} \times \frac{0.030}{[CO_3^{2-}]}$$

We will use this equation for each of the two boundary values of $[CO_3^{2-}]$ to calculate the corresponding two values of $[H^+]^2$. Once we have them, we can readily determine $[H^+]$ and pH.

For magnesium carbonate: To *prevent* the precipitation of $MgCO_3$, $[CO_3^{2-}]$ must be no higher than 3.5×10^{-7} *M*, so $[H^+]^2$ must not be less than

$$[H^+]^2 = 2.4 \times 10^{-17} \times \frac{0.030}{6.8 \times 10^{-17}} = 1.1 \times 10^{-12}$$
$$[H^+] = 1.0 \times 10^{-6}\ M$$

This corresponds to a pH of 6.00. At a higher (more basic) pH, magnesium carbonate precipitates. Thus, pH $\leq$ 6.00 prevents the precipitation of $MgCO_3$.

For strontium carbonate: To have a saturated solution of $SrCO_3$ with $[Sr^{2+}] = 0.10\ M$, the value of $[CO_3^{2-}]$ would be $5.6 \times 10^{-9}\ M$, as we calculated previously. This corresponds to a value of $[H^+]^2$ found as follows:

$$[H^+]^2 = 2.4 \times 10^{-17} \times \frac{0.030}{5.6 \times 10^{-9}} = 1.3 \times 10^{-10}$$

$$[H^+] = 1.1 \times 10^{-5}\ M$$

$$\text{pH} = 4.95$$

To cause $SrCO_3$ to precipitate, the $[CO_3^{2-}]$ would have to be higher than $5.6 \times 10^{-9}\ M$, and that would require that $[H^+]$ be *less than* $1.1 \times 10^{-5}\ M$. If $[H^+]$ were less than $1.1 \times 10^{-5}\ M$, the pH would have to be higher than 4.95. Thus, to cause $SrCO_3$ to precipitate from the given solution, pH $>$ 4.95.

In summary, when the pH of the given solution is kept above 4.95 and less than or equal to 6.00, Sr^{2+} will precipitate as $SrCO_3$, but Mg^{2+} will remain dissolved.

■ **Is the Answer Reasonable?** The only way to be sure of the answer is to go back over the reasoning and the calculations. However, there is a sign that the answer is probably correct. Notice that the two K_{sp} values are not vastly different—they differ by just a factor of about 40. Therefore, it's not surprising that to achieve separation we would have to keep the pH within a rather narrow range (from 4.95 to 6.00).

Practice Exercises

18.18 | The K_{sp} for barium oxalate, BaC_2O_4, is 1.2×10^{-7} and for oxalic acid, $H_2C_2O_4$, $K_{a_1} = 6.0 \times 10^{-2}$ and $K_{a_2} = 6.1 \times 10^{-5}$. If a solution containing 0.10 M $H_2C_2O_4$ and 0.050 M $BaCl_2$ is prepared, what must the minimum H^+ concentration be in the solution to prevent the formation of a BaC_2O_4 precipitate? (*Hint*: Work with a combined K_a expression for $H_2C_2O_4$.)

18.19 | A solution contains calcium nitrate and nickel nitrate, each at a concentration of 0.10 M. Carbon dioxide is to be bubbled in to make its concentration equal 0.030 M. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other?

Separating Metal Ions: Qualitative Analysis

The method for determining what elements are present in a sample is called *qualitative analysis*. Metal ions can be separated and isolated by selective precipitation with different anions at different pH values. The metal cations have been divided into five groups, depending on the solubilities of their compounds.

The first group is the chloride group, which will precipitate Pb^{2+}, Hg_2^{2+}, and Ag^+. This precipitation reaction is carried out by adding HCl to the solution. To precipitate the next group, the concentration of HCl is brought to 0.3 M and H_2S is added. All of the acid-insoluble sulfides will precipitate (Hg^{2+}, Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Sn^{2+} from Table 18.2, as well as Bi^{3+}, As^{3+}, and Sb^{3+}). The third group is precipitated by the addition of NaOH, which will make the solution basic. The compounds MnS, FeS, NiS, CoS, and ZnS will precipitate as base-insoluble sulfides along with the hydroxides $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$. For the fourth group, CO_3^{2-} is added to the solution and the following carbonates are precipitated: $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$. The final group is the metal cations that are completely soluble—namely, Na^+, K^+, and NH_4^+. This scheme is summarized in Figure 18.6.

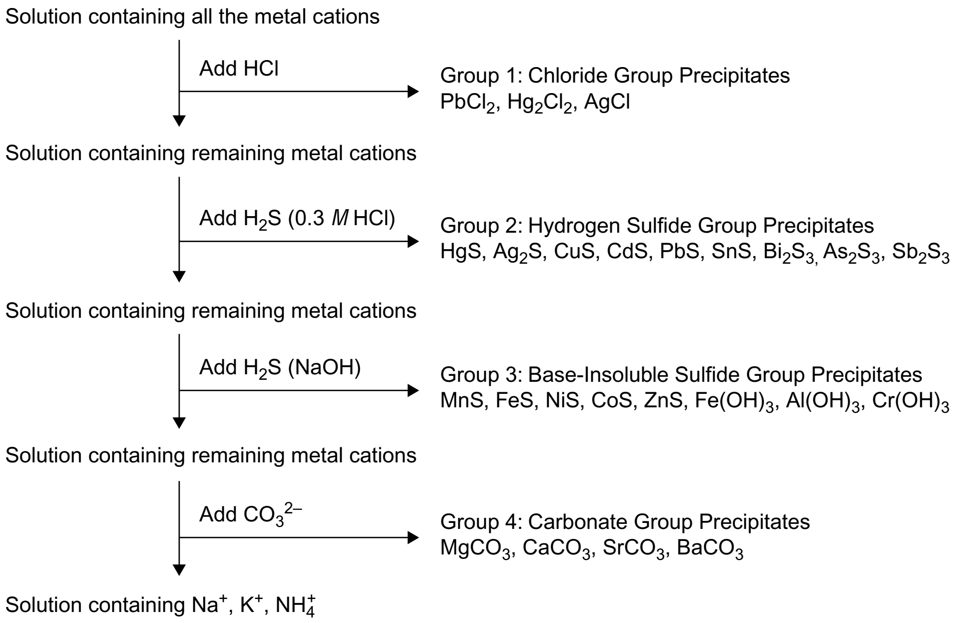

Solution containing all the metal cations
Add HCl
Group 1: Chloride Group Precipitates
$PbCl_2$, Hg_2Cl_2, AgCl
Solution containing remaining metal cations
Add H_2S (0.3 *M* HCl)
Group 2: Hydrogen Sulfide Group Precipitates
HgS, Ag_2S, CuS, CdS, PbS, SnS, Bi_2S_3, As_2S_3, Sb_2S_3
Solution containing remaining metal cations
Add H_2S (NaOH)
Group 3: Base-Insoluble Sulfide Group Precipitates
MnS, FeS, NiS, CoS, ZnS, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$
Solution containing remaining metal cations
Add CO_3^{2-}
Group 4: Carbonate Group Precipitates
$MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$
Solution containing Na^+, K^+, NH_4^+

Figure 18.6 | **Outline of the qualitative analysis scheme.**

18.4 | Equilibria Involving Complex Ions

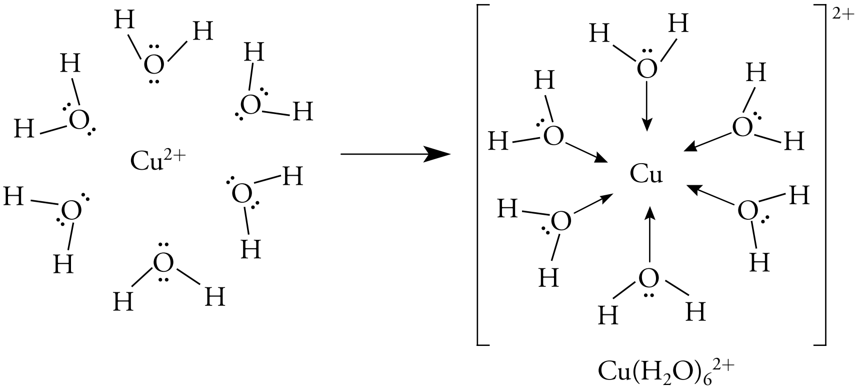
Formation of Complex Ions

In our previous discussions of metal-containing compounds, we left you with the impression that the only kinds of bonds in which metals are ever involved are ionic bonds. For some metals, like the alkali metals of Group 1A, this is close enough to the truth to warrant no modifications. However, for many other metal ions, especially those of the transition metals and the post-transition metals, it is not. This is because the ions of many of these metals are able to behave as Lewis acids (i.e., as electron pair acceptors in the formation of coordinate covalent bonds). Thus, by participating in Lewis acid–base reactions they become *covalently* bonded to other atoms. Copper(II) ion is a typical example.

In aqueous solutions of copper(II) salts, such as $CuSO_4$ or $Cu(NO_3)_2$, the copper is not present as simple Cu^{2+} ions. Instead, each Cu^{2+} ion becomes bonded to six water molecules to give a pale blue ion with the formula $Cu(H_2O)_6^{2+}$ (see Figure 18.7). We call this species a **complex ion** because it is composed of a number of simpler species (i.e., it is *complex*, not simple). The chemical equation for the formation of the $Cu(H_2O)_6^{2+}$ ion is

$$Cu^{2+} + 6H_2O \longrightarrow Cu(H_2O)_6^{2+}$$

which can be diagrammed using Lewis structures as follows:



$Cu(H_2O)_6^{2+}$

Figure 18.7 | **The complex ion of Cu^{2+} and water.** A solution containing copper sulfate has a blue color because it contains the complex ion $Cu(H_2O)_6^{2+}$. *(Andy Washnik)*

■ Recall that a *Lewis base* is an electron pair donor in the formation of a coordinate covalent bond.

As you can see in this analysis, the Cu^{2+} ion accepts pairs of electrons from the water molecules, so Cu^{2+} is a Lewis acid and the water molecules are each Lewis bases.

The number of complex ions formed by metals, especially the transition metals, is enormous, and the study of the properties, reactions, structures, and bonding in complex ions like $Cu(H_2O)_6{}^{2+}$ has become an important specialty within chemistry. We will provide a more complete discussion of them in Chapter 22. For now, we will introduce you to some of the terminology that we use in describing these substances.

A Lewis base that attaches itself to a metal ion is called a **ligand** (from the Latin *ligare*, meaning "to bind"). Ligands can be neutral molecules with unshared pairs of electrons (e.g., H_2O), or they can be anions (e.g., Cl^- or OH^-). The atom in the ligand that actually provides the electron pair is called the **donor atom**, and the metal ion is the **acceptor**. The result of combining a metal ion with one or more ligands is a *complex ion*, or simply just a **complex**. The word "complex" avoids problems when the particle formed is electrically neutral, as sometimes happens. Compounds that contain complex ions are generally referred to as **coordination compounds** because the bonds in a complex ion can be viewed as coordinate-covalent bonds. Sometimes the complex itself is called a **coordination complex.**

In an aqueous solution, the formation of a complex ion is really a reaction in which water molecules are replaced by other ligands. Thus, when NH_3 is added to a solution of copper ion, the water molecules in the $Cu(H_2O)_6{}^{2+}$ ion are replaced stepwise by molecules of NH_3 until the deeply blue complex $Cu(NH_3)_4{}^{2+}$ is formed (Figure 18.8). Each successive reaction is an equilibrium, so the entire chemical system involves many species and is quite complicated. Fortunately, when the ligand concentration is *large* relative to that of the metal ion, the concentrations of the intermediate complexes are very small and we can work only with the *overall* reaction for the formation of the final complex. Our study of complex ion equilibria will be limited to these situations. The equilibrium equation for the formation of $Cu(NH_3)_4{}^{2+}$, therefore, can be written as though the complex forms in one step.

■ According to Le Châtelier's principle, when the concentration of ammonia is high, the position of equilibrium in this reaction is shifted far to the right, so effectively all complex ions with water molecules are changed to those with ammonia molecules.

$$Cu(H_2O)_6{}^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) + 6H_2O$$

We will simplify this equation for the purposes of dealing quantitatively with the equilibria by omitting the water molecules. (As in Chapter 15, it is appropriate to do this because the concentration of H_2O in aqueous solutions is taken to be effectively a constant and need not be included in mass action expressions.) In simplified form, we write the preceding equilibrium as follows:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$$

We have two goals here—namely, to study such equilibria themselves and to learn how they can be used to influence the solubilities of metal ion salts.

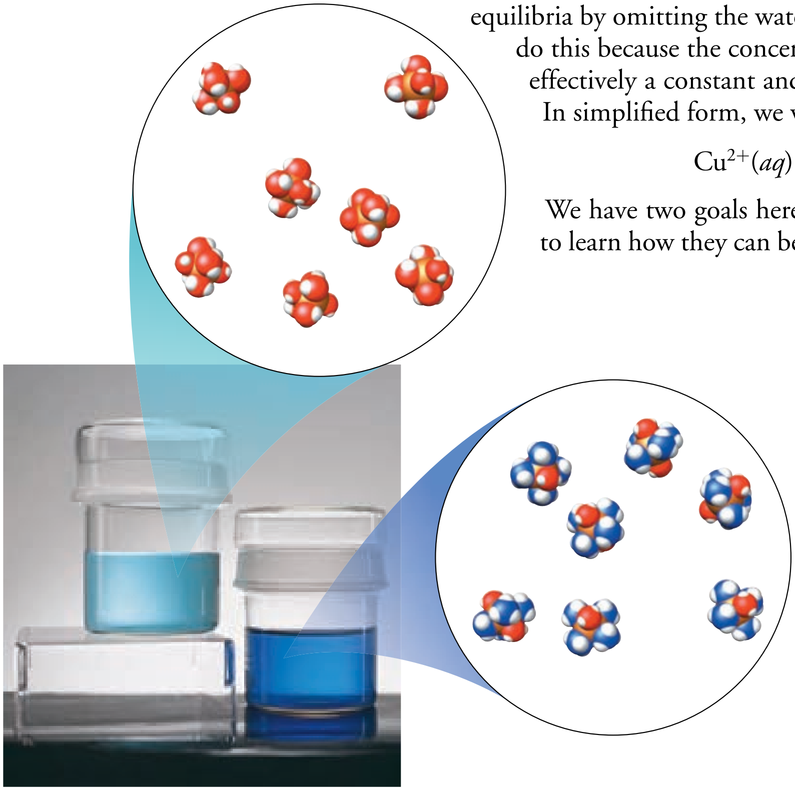


Figure 18.8 | **The complex ion of Cu^{2+} and ammonia.** Ammonia molecules displace water molecules from $Cu(H_2O)_6{}^{2+}$ (left) to give the deep blue $Cu(NH_3)_4{}^{2+}$ ion (right). In the molecular view we show two water molecules that are also weakly attached to the copper ion in the $Cu(NH_3)_4{}^{2+}$ cation. *(Andy Washnik)*

Formation Constants

When the chemical equation for the equilibrium is written so that the complex ion is the product, the equilibrium constant for the reaction is called the **formation constant, K_{form}.** The equilibrium law for the formation of $Cu(NH_3)_4^{2+}$ in the presence of excess NH_3, for example, is

$$\frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = K_{\text{form}}$$

Formation constants of complex ions

Sometimes this equilibrium constant is called the **stability constant**. The larger its value, the greater is the concentration of the complex at equilibrium, and so the more stable is the complex.

Table 18.3 provides several more examples of complex ion equilibria and their associated equilibrium constants. (Additional examples are in Appendix C.) The most stable complex in the table, $Co(NH_3)_6^{3+}$, has the largest value of K_{form}.

Instability Constants

Some chemists prefer to describe the relative stabilities of complex ions differently. Their approach focuses attention on the *breakdown* of the complex, not its formation. Therefore, the associated equilibrium equation is written as the reverse of the formation of the complex. The equilibrium for the copper–ammonia complex would be written as follows, for example:

$$Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$$

The equilibrium constant for this equilibrium is called the **instability constant, K_{inst}:**

$$K_{\text{inst}} = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = \frac{1}{K_{\text{form}}}$$

Notice that K_{inst} is the reciprocal of K_{form}. The K_{inst} is called an *instability* constant because the larger its value is, the more *unstable* the complex is. The data in the last column of Table 18.3 show this. The least stable complex in the table, $Co(NH_3)_6^{2+}$, has the largest value of K_{inst}.

Table 18.3 Formation Constants and Instability Constants for Some Complex Ions

Ligand	Equilibrium	K_{form}	K_{inst}
NH_3	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.6×10^{7}	6.3×10^{-8}
	$Co^{2+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{2+}$	5.0×10^{4}	2.0×10^{-5}
	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	4.6×10^{33}	2.2×10^{-34}
	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	1.1×10^{13}	9.1×10^{-14}
	$Hg^{2+} + 4NH_3 \rightleftharpoons Hg(NH_3)_4^{2+}$	1.8×10^{19}	5.6×10^{-20}
F^-	$Al^{3+} + 6F^- \rightleftharpoons AlF_6^{3-}$	1×10^{20}	1×10^{-20}
	$Sn^{4+} + 6F^- \rightleftharpoons SnF_6^{2-}$	1×10^{25}	1×10^{-25}
Cl^-	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	5.0×10^{15}	2.0×10^{-16}
Br^-	$Hg^{2+} + 4Br^- \rightleftharpoons HgBr_4^{2-}$	1.0×10^{21}	1.0×10^{-21}
I^-	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	1.9×10^{30}	5.3×10^{-31}
CN^-	$Fe^{2+} + 6CN^- \rightleftharpoons Fe(CN)_6^{4-}$	1.0×10^{24}	1.0×10^{-24}
	$Fe^{3+} + 6CN^- \rightleftharpoons Fe(CN)_6^{3-}$	1.0×10^{31}	1.0×10^{-31}

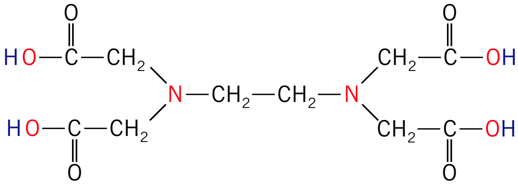
CHEMISTRY OUTSIDE THE CLASSROOM | 18.1

No More Soap Scum—Complex Ions and Solubility

A problem that has plagued homeowners with hard water—water that contains low concentrations of divalent cations, especially Ca^{2+}—is the formation of insoluble deposits of "soap scum" as well as "hard water spots" on surfaces such as shower tiles, shower curtains, and bathtubs. These deposits form when calcium ions interact with large anions in soap to form precipitates and also when hard water that contains bicarbonate ion evaporates, causing the precipitation of calcium carbonate, $CaCO_3$.

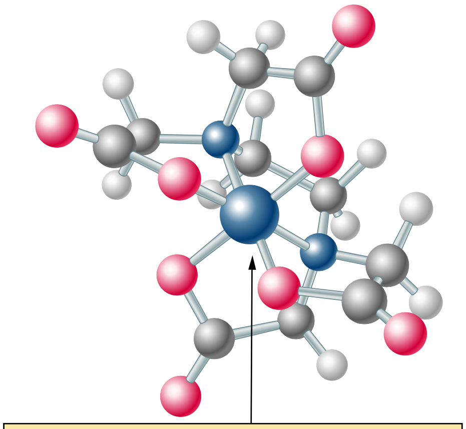
$$Ca^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow CaCO_3(s) + CO_2(g) + H_2O$$

A variety of consumer products are sold that contain ingredients intended to prevent these precipitates from forming, and they accomplish this by forming complex ions with calcium ions, which has the effect of increasing the solubilities of the soap scum and calcium carbonate deposits. A principal ingredient in these products is an organic compound called *ethylenediaminetetraacetic* acid (mercifully abbreviated *EDTA*). The structure of the compound, which is also abbreviated as H_4EDTA to emphasize that it contains four acidic hydrogens that are part of carboxyl groups, is



H_4EDTA
Acidic hydrogens are shown in blue,
donor atoms are shown in red.

This molecule is an excellent complex-forming ligand; it contains a total of *six* donor atoms (in red) that can bind to a metal ion, enabling the ligand to wrap itself around the metal ion as illustrated above, right. (The usual colors are used to identify the various elements in the ligand.)



A metal ion surrounded octahedrally by all six donor atoms if H_4EDTA loses all of the acidic hydrogens.

One consumer product, called Clean Shower (Figure 1), contains H_4EDTA along with substances called surfactants. When the EDTA binds with calcium ions, it releases just two H^+ ions,

$$H_4EDTA(aq) + Ca^{2+}(aq) \longrightarrow CaH_2EDTA(aq) + 2H^+(aq)$$

The H^+ combine with anions of the soap to form neutral organic compounds called fatty acids that are usually not water soluble. The surfactants in the product, however, enable the fatty acids to dissolve, preventing the formation of precipitates. The Clean Shower product is sprayed on the wet walls after taking a shower, forming the products just described. The next time you take a shower, the water washes away the soluble products, keeping soap scum from building up and keeping the shower walls clean.

CLEAN SHOWER

Figure 1 The product Clean Shower contains EDTA, which prevents the formation of soap scum and hard water spots in showers and on bathtubs. *(Andy Washnik)*

18.5 | Complexation and Solubility

The silver halides are extremely insoluble salts. The K_{sp} of AgBr at 25 °C, for example, is only 5.4×10^{-13}. In a saturated aqueous solution, the concentration of each ion of AgBr is only 7.3×10^{-7} mol L^{-1}. Suppose that we start with a saturated solution in which undissolved AgBr is present and equilibrium exists. Now, suppose that we begin to add aqueous ammonia to the system. Because NH_3 molecules bind strongly to silver ions, they begin to form $Ag(NH_3)_2^+$ with the trace amount of Ag^+ ions initially in solution. The reaction is

Complex ion equilibrium:

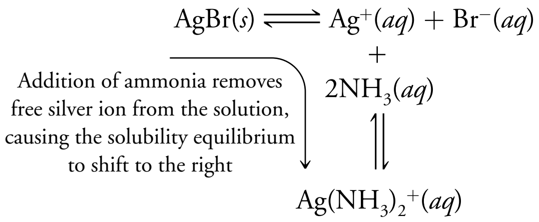
$$\mathrm{Ag^+}(aq) + 2\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^+(aq) \qquad K_{\mathrm{form}} = 1.6 \times 10^7$$

Because the forward reaction removes *uncomplexed* $\mathrm{Ag^+}$ ions from solution, it upsets the solubility equilibrium:

Solubility equilibrium:

$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Br^-}(aq) \qquad K_{\mathrm{sp}} = 5.4 \times 10^{-13}$$

By withdrawing uncomplexed $\mathrm{Ag^+}$ ions, the ammonia causes the solubility equilibrium to shift to the right to generate more $\mathrm{Ag^+}$ ions from AgBr(s). The way the two equilibria are related can be viewed as follows:


AgBr(s) ⇌ Ag+(aq) + Br−(aq)
+
2NH3(aq)
Ag(NH3)2+(aq)
Addition of ammonia removes free silver ion from the solution, causing the solubility equilibrium to shift to the right

Thus, adding ammonia causes more AgBr(s) to dissolve—an example of Le Châtelier's principle at work. Our example illustrates the following general phenomenon:

> The solubility of a slightly soluble salt increases when one of its ions can be changed to a soluble complex ion.

To analyze what happens, lets put the two equilibria together:

$$\begin{array}{ll} \textit{Complex ion equilibrium:} & \mathrm{Ag^+}(aq) + 2\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^+(aq) \\ \textit{Solubility equilibrium:} & \mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Br^-}(aq) \\ \hline \textit{Sum of equilibria:} & \mathrm{AgBr}(s) + 2\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^+(aq) + \mathrm{Br^-}(aq) \end{array}$$

The equilibrium constant for the net overall reaction is written in the usual way. Again, the term for [AgBr(s)] is omitted because it refers to a solid and so has a constant value:

$$K_c = \frac{[\mathrm{Ag(NH_3)_2}^+][\mathrm{Br^-}]}{[\mathrm{NH_3}]^2}$$

Because we have added two equations to obtain a third equation, K_c for this expression is the product of K_{form} and K_{sp}. The values for K_{form} for $\mathrm{Ag(NH_3)_2}^+$ and K_{sp} for AgBr are known, so by multiplying the two, we find the overall value of K_c for the silver bromide–ammonia system.

■ Recall that when equilibrium equations are added, their equilibrium constants are multiplied.

$$\begin{aligned} K_c &= K_{\mathrm{form}} \times K_{\mathrm{sp}} \\ K_c &= (1.6 \times 10^7)(5.4 \times 10^{-13}) \\ &= 8.0 \times 10^{-6} \end{aligned}$$

This approach thus gives us a way to calculate the solubility of a sparingly soluble salt when a substance able to form a complex with the metal ion is put into its solution. Example 18.11 shows how this works.

Example 18.11

Calculating the Solubility of a Slightly Soluble Salt in the Presence of a Ligand

How many moles of AgBr can dissolve in 1.0 L of 1.0 M NH_3?

■ **Analysis:** Silver bromide is insoluble in water, but with the addition of NH_3, more AgBr can be dissolved. This question is asking us to use the K_{form} and the K_{sp} together to determine the amount of AgBr dissolved in water.

■ **Assembling the Tools:** A few preliminaries have to be done before we can take advantage of a concentration table. We need the overall balanced chemical equation and its associated equation for the equilibrium constant, which serve as our tools for dealing with these kinds of problems. The overall equilibrium is

$$AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{\ +}(aq) + Br^-(aq)$$

The equation for K_c is

$$K_c = \frac{[Ag(NH_3)_2^{\ +}][Br^-]}{[NH_3]^2} = 8.0 \times 10^{-6} \qquad \text{(as calculated earlier)}$$

Next, we will need to use the concentration table. To do this, we imagine we are adding solid AgBr to the ammonia solution.

Before any reaction takes place, the concentration of NH_3 is 1.0 M and the concentration of $Ag(NH_3)_2^{\ +}$ is zero. The concentration of Br^- is also zero, because there is none of it in the ammonia solution.

If we define x as the molar solubility of the AgBr in the solution, then the concentrations of $Ag(NH_3)_2^{\ +}$ and Br^- both increase by x and the concentration of ammonia decreases by $2x$ (because of the coefficient of NH_3 in the balanced chemical equation).

The equilibrium values are obtained as usual by adding the initial and change rows. However, we need to note that letting the concentration of Br^- equal that of $Ag(NH_3)_2^{\ +}$ is valid because *and only because* K_{form} is such a large number. Essentially *all* Ag^+ ions that do dissolve from the insoluble AgBr are changed into the complex ion. There are relatively few uncomplexed Ag^+ ions in the solution, so the number of $Ag(NH_3)_2^{\ +}$ and Br^- ions in the solution are very nearly the same.

■ **Solution:** The concentration table is as follows.

	$AgBr(s)$	$+$	$2NH_3(aq)$	$\rightleftharpoons$	$Ag(NH_3)_2^{\ +}(aq)$	$+$	$Br^-(aq)$
Initial concentrations (M)			1.0		0		0
Change in concentrations caused by NH_3 (M)			$-2x$		$+x$		$+x$
Equilibrium concentrations (M)			$(1.0 - 2x)$		x		x

We've done all the hard work. Now all we need to do is substitute the values in the last row of the concentration table into the equation for K_c,

$$K_c = \frac{(x)(x)}{(1.0 - 2x)^2} = 8.0 \times 10^{-6}$$

This can be solved analytically by taking the square root of both sides, which gives

$$\frac{(x)}{(1.0 - 2x)} = \sqrt{8.0 \times 10^{-6}} = 2.8 \times 10^{-3}$$

Solving for x and rounding to the correct number of significant figures gives

$$x = 2.8 \times 10^{-3}$$

Because we've defined x as the molar solubility of AgBr in the ammonia solution, we can say that 2.8×10^{-3} mol of AgBr dissolves in 1.0 L of 1.0 M NH_3. (This is not very much, but in contrast, only 7.1×10^{-7} mol of AgBr dissolves in 1.0 L of pure water. Thus, AgBr is nearly 4000 times more soluble in the 1.0 M NH_3 than in pure water.)

■ **Is the Answer Reasonable?** Everything depends on the reasoning used in preparing the concentration table, particularly letting $-2x$ represent the change in the concentration of NH_3 as a result of the presence of AgBr and the formation of the complex. If you are comfortable with this, then the calculation should be straightforward.

Practice Exercises

18.20 | Calculate the solubility of silver chloride in 0.10 M NH_3 and compare it with its solubility in pure water. Refer to Table 18.1 for the K_{sp} for AgCl. (*Hint*: Assume that all of the Ag^+ from the AgCl becomes incorporated into $Ag(NH_3)_2{}^+$.)

18.21 | How many moles of NH_3 have to be added to 1.0 L of water to dissolve 0.20 mol of AgCl? The complex ion $Ag(NH_3)_2{}^+$ forms.

Summary

Solubility Equilibria for Salts. The mass action expression for a solubility equilibrium of a salt is called the **ion product**. It equals the product of the molar concentrations of its ions, each raised to a power equal to the subscript of the ion in the salt's formula. At a given temperature, the value of the ion product, Q, in a *saturated* solution of the salt equals a constant called the **solubility product constant** or $\boldsymbol{K_{sp}}$.

For solubility equilibria, the *common ion effect* is the ability of an ion of a soluble salt to suppress the solubility of a sparingly soluble compound that has the same (the "common") ion.

If soluble salts are mixed together in the same solution, a cation of one and an anion of another will precipitate if the ion product, Q, exceeds the solubility product constant of the salt formed from them.

Selective Precipitation. Metal sulfides are vastly more soluble in an acidic solution than in water. To express their solubility equilibria in acid, the **acid solubility constant** or $\boldsymbol{K_{spa}}$ is used. Several metal sulfides have such low values of K_{spa} that they are insoluble even at low pH. These **acid-insoluble sulfides** can thus be selectively separated from the **base-insoluble sulfides** by making the solution both quite acidic as well as saturated in H_2S. By adjusting the pH, salts of other weak acids, like the carbonate salts, can also be selectively precipitated.

Complex Ions of Metals. **Coordination compounds** contain **complex ions** (also called **complexes** or **coordination complexes**) formed from a metal ion and a number of ligands. **Ligands** are Lewis bases (electron pair donors) and may be electrically neutral or negatively charged. Water and ammonia are common neutral ligands. Metal ions often act as electron pair acceptors (i.e., as Lewis acids). The equilibrium constant for the formation of a metal–ligand complex in the presence of an excess of ligand is called the **formation constant,** $\boldsymbol{K_{form}}$, of the complex. The larger the value of K_{form}, the more stable is the complex. Salts whose cations form stable complexes, like Ag^+ salts whose cation forms a stable complex with ammonia, $Ag(NH_3)_2{}^+$, are made more soluble when the ligand is present.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Solubility product constant, $\boldsymbol{K_{sp}}$ (page 831)

We use K_{sp} to calculate the molar solubility of a salt either in pure water or in a solution that contains a common ion. Comparing K_{sp} with the ion product of a potential precipitating salt permits us to decide whether a precipitate will form.

Molar solubility (page 833)

This is used for calculating the value of K_{sp} for a salt. When calculating the solubility of a salt from K_{sp}, we let x represent the molar solubility in the concentration table.

Concentration table (page 833)

The concentration tables are the same as the concentration table tool in Chapter 15, only we are using them for insoluble salts in this chapter.

Predicting precipitation (page 841)

Compare Q with K_{sp} to determine whether a precipitate will form:

$$Q > K_{sp}, \text{ a precipitate forms}$$
$$Q \leq K_{sp}, \text{ a precipitate does } \textit{not} \text{ form}$$

Acid solubility product constant, K_{spa} (page 847)

Use K_{spa} data to calculate the solubility of a metal sulfide at a given pH. We can use K_{spa} data for two or more metal sulfides to calculate the pH at which one will selectively precipitate from a solution saturated in H_2S.

Combined K_a expression for a diprotic acid (page 852)

Combining expressions for K_{a_1} and K_{a_2} for a diprotic acid, H_2A, yields the equation

$$\frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_a = K_{a_1} \times K_{a_2}$$

This equation can be used if (and only if) we know two of the three quantities in the combined mass action expression. This is a useful tool when working problems involving the selective precipitation of salts of diprotic acids where the concentration of the anion A^{2-} is controlled by adjusting the pH of the solution.

Formation constants of complex ions (page 857)

We can use them to make judgments concerning the relative stabilities of complexes. Along with K_{sp} values, we can use formation constants of complexes to determine the solubility of a sparingly soluble salt in a solution containing a ligand that's able to form a complex with the cation of the salt.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Solubility Products

18.1 What is the difference between an *ion product* and an *ion product constant*?

18.2 Use the following equilibrium to demonstrate why the K_{sp} expression does not include the concentration of $Ba_3(PO_4)_2$ in the denominator:

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3-}(aq)$$

18.3 What is the common ion effect? How does Le Châtelier's principle explain it? Use the solubility equilibrium for AgCl and the addition of NaCl to the solution to illustrate the common ion effect.

18.4 With respect to K_{sp}, what conditions must be met if a precipitate is going to form in a solution?

18.5 What limits the accuracy and reliability of solubility calculations based on K_{sp} values?

18.6 Why do we *not* use K_{sp} values for soluble salts such as NaCl?

Selective Precipitation

18.7 Potassium oxide is readily soluble in water, but the resulting solution contains essentially no oxide ion. Explain, using an equation, what happens to the oxide ion.

18.8 What chemical reaction takes place when solid sodium sulfide is dissolved in water? Write the chemical equation.

18.9 Consider cobalt(II) sulfide.

(a) Write its solubility equilibrium and K_{sp} equation for a saturated solution in water. (Remember: There is no free sulfide ion in the solution.)

(b) Write its solubility equilibrium and K_{spa} equation for a saturated solution in aqueous acid.

18.10 Use Le Châtelier's principle to explain how adjusting the pH makes it possible to control the concentration of $C_2O_4^{2-}$ in a solution of oxalic acid, $H_2C_2O_4$.

18.11 Suppose you wanted to control the PO_4^{3-} concentration in a solution of phosphoric acid by controlling the pH of the solution. If you assume you know the H_3PO_4 concentration, what combined equation would be useful for this purpose?

18.12 If you had a solution with Ag^+, Co^{2+}, and Cu^{2+}, how could you separate the metal ions by selective precipitation?

Simultaneous and Complex Ion Equilibria

18.13 A solution of $MgBr_2$ can be changed to a solution of $MgCl_2$ by adding $AgCl(s)$ and stirring the mixture well. In terms of the equilibria involved, explain how this happens.

18.14 On the basis of Le Châtelier's principle, explain how the addition of solid NH_4Cl to a beaker containing solid $Mg(OH)_2$ in contact with water is able to cause the $Mg(OH)_2$ to dissolve. Write equations for *all* of the chemical equilibria that exist in the solution after the addition of the NH_4Cl.

18.15 Using Le Châtelier's principle, explain how the addition of aqueous ammonia dissolves silver chloride. If HNO_3 is added after the AgCl has dissolved in the NH_3 solution, it causes AgCl to re-precipitate. Explain why.

18.16 For $PbCl_3^-$, $K_{form} = 2.5 \times 10^1$. If a solution containing this complex ion is diluted with water, $PbCl_2$ precipitates. Write the equations for the equilibria involved and use them together with Le Châtelier's principle to explain how this happens.

18.17 Which of the following will be more soluble if acid is added to the mixture? Will adding base increase the solubility of any of these? Are any of their solubilities independent of the pH of the solution? **(a)** ZnS, **(b)** $Ca(OH)_2$, **(c)** $MgCO_3$, **(d)** AgCl, **(e)** PbF_2

Review Problems

Solubility Products

18.18 Write the K_{sp} expressions for each of the following compounds:

(a) CaF_2 **(c)** $PbSO_4$ **(e)** PbI_2

(b) Ag_2CO_3 **(d)** $Fe(OH)_3$ **(f)** $Cu(OH)_2$

18.19 Write the K_{sp} expressions for each of the following compounds:

(a) AgI **(c)** $PbCrO_4$ **(e)** $ZnCO_3$

(b) Ag_3PO_4 **(d)** $Al(OH)_3$ **(f)** $Zn(OH)_2$

Determining K_{sp}

18.20 In water, the solubility of lead(II) chloride is 0.016 *M*. Use this information to calculate the value of K_{sp} for $PbCl_2$.

18.21 The solubility of zinc oxalate is 7.9×10^{-3} *M*. Calculate the K_{sp} for ZnC_2O_4.

18.22 Barium sulfate is so insoluble that it can be swallowed without significant danger, even though Ba^{2+} is toxic. At 25 °C, 1.00 L of water dissolves only 0.00245 g of $BaSO_4$. Calculate the molar solubility and K_{sp} for $BaSO_4$.

18.23 A student found that a maximum of 0.800 g silver acetate is able to dissolve in 100.0 mL of water. What is the molar solubility and the K_{sp} for this salt?

OH **18.24** A student evaporated 100.0 mL of a saturated BaF_2 solution and found the solid BaF_2 she recovered weighed 0.132 g. From these data, calculate K_{sp} for BaF_2.

18.25 A student prepared a saturated solution of $CaCrO_4$ and found that when 156 mL of the solution was evaporated, 0.649 g of $CaCrO_4$ was left behind. What is the value of K_{sp} for this salt?

18.26 At 25 °C, the molar solubility of silver phosphate is 1.8×10^{-5} mol L^{-1}. Calculate K_{sp} for this salt.

18.27 The molar solubility of barium phosphate in water at 25 °C is 1.4×10^{-8} mol L^{-1}. What is the value of K_{sp} for this salt?

Using K_{sp} to Calculate Solubilities

18.28 Which compound is more soluble in water, $ZnCO_3$ or $MgCO_3$?

18.29 Which compound is more soluble in water, $BaSO_4$ or $SrCO_3$?

18.30 What is the molar solubility of $PbBr_2$ in water?

18.31 What is the molar solubility of Ag_2CrO_4 in water?

18.32 Calculate the molar solubility of $Zn(CN)_2$ in water. (Ignore the reaction of the CN^- ion with water.)

18.33 Calculate the molar solubility of PbF_2 in water. (Ignore the reaction of the F^- ion with water.)

18.34 At 25 °C, the value of K_{sp} for LiF is 1.8×10^{-3}, and that for BaF_2 is 1.7×10^{-6}. Which salt, LiF or BaF_2, has the larger molar solubility in water? Calculate the solubility of each in units of mol L^{-1}.

18.35 At 25 °C, the value of K_{sp} for AgCN is 6.0×10^{-17} and that for $Zn(CN)_2$ is 3×10^{-16}. In terms of grams per 100 mL of solution, which salt is more soluble in water?

18.36 A salt whose formula is MX has a K_{sp} equal to 3.2×10^{-10}. Another sparingly soluble salt, MX_3, must have what value of K_{sp} if the molar solubilities of the two salts are to be identical?

18.37 A salt having a formula of the type M_2X_3 has $K_{sp} = 2.2 \times 10^{-20}$. Another salt, M_2X, has to have what K_{sp} value if M_2X has twice the molar solubility of M_2X_3?

18.38 Calcium sulfate is found in plaster. At 25 °C the value of K_{sp} for $CaSO_4$ is 4.9×10^{-5}. What is the calculated molar solubility of $CaSO_4$ in water?

18.39 Chalk is $CaCO_3$, and at 25 °C its $K_{sp} = 3.4 \times 10^{-9}$. What is the molar solubility of $CaCO_3$? How many grams of $CaCO_3$ dissolve in 0.100 L of aqueous solution? (Ignore the reaction of CO_3^{2-} with water.)

Common Ion Effect

18.40 It was found that the molar solubility of $BaSO_3$ in 0.10 *M* $BaCl_2$ is 8.0×10^{-6} *M*. What is the value of K_{sp} for $BaSO_3$?

18.41 The molar solubility of Ag_2CrO_4 in 0.10 *M* Na_2CrO_4 is 1.7×10^{-6} *M*. What is the value of K_{sp} for Ag_2CrO_4?

ILW **18.42** Copper(I) chloride has $K_{sp} = 1.7 \times 10^{-7}$. Calculate the molar solubility of copper(I) chloride in **(a)** pure water, **(b)** 0.0200 *M* HCl solution, **(c)** 0.200 *M* HCl solution, and **(d)** 0.150 *M* $CaCl_2$ solution.

18.43 Gold(III) chloride has $K_{sp} = 3.2 \times 10^{-25}$. Calculate the molar solubility of gold(III) chloride in **(a)** pure water, **(b)** 0.010 *M* HCl solution, **(c)** 0.010 *M* $MgCl_2$ solution, and **(d)** 0.010 *M* $Au(NO_3)_3$ solution.

18.44 Calculate the molar solubility of $Mg(OH)_2$ in a solution that is basic with a pH of 12.50.

18.45 Calculate the molar solubility of $Al(OH)_3$ in a solution that is slightly basic with a pH of 9.50.

18.46 What is the highest concentration of Pb^{2+} that can exist in a solution of 0.10 *M* HCl?

18.47 Will lead(II) bromide be less soluble in 0.10 *M* $Pb(C_2H_3O_2)_2$ or in 0.10 *M* NaBr?

18.48 Calculate the molar solubility of Ag_2CrO_4 at 25 °C in **(a)** 0.200 *M* $AgNO_3$ and **(b)** 0.200 *M* Na_2CrO_4. For Ag_2CrO_4 at 25 °C, $K_{sp} = 1.1 \times 10^{-12}$.

18.49 What is the molar solubility of $Mg(OH)_2$ in **(a)** 0.20 *M* NaOH and **(b)** 0.20 *M* $MgSO_4$? For $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{-12}$.

***18.50** In an experiment, 2.20 g of NaOH(*s*) is added to 250 mL of 0.10 *M* $FeCl_2$ solution. What mass of $Fe(OH)_2$ will be formed? What will the molar concentration of Fe^{2+} be in the final solution?

***18.51** Suppose that 1.75 g of NaOH(*s*) is added to 250 mL of 0.10 *M* $NiCl_2$ solution. What mass, in grams, of $Ni(OH)_2$ will be formed? What will be the pH of the final solution? For $Ni(OH)_2$, $K_{sp} = 5.5 \times 10^{-16}$.

18.52 What is the molar solubility of $Fe(OH)_2$ in a buffer that has a pH of 9.50?

18.53 What is the molar solubility of $Ca(OH)_2$ in **(a)** 0.10 *M* $CaCl_2$ and **(b)** 0.10 *M* NaOH?

Precipitation

18.54 Does a precipitate of $PbCl_2$ form when 0.0150 mol of $Pb(NO_3)_2$ and 0.0120 mol of NaCl are dissolved in 1.00 L of solution?

18.55 Silver acetate, $AgC_2H_3O_2$, has $K_{sp} = 2.3 \times 10^{-3}$. Does a precipitate form when 0.015 mol of $AgNO_3$ and 0.25 mol of $Ca(C_2H_3O_2)_2$ are dissolved in a total volume of 1.00 L of solution?

ILW **18.56** Does a precipitate of $PbBr_2$ form if 50.0 mL of 0.0100 *M* $Pb(NO_3)_2$ is mixed with **(a)** 50.0 mL of 0.0100 *M* KBr and **(b)** 50.0 mL of 0.100 *M* NaBr?

18.57 Would a precipitate of silver acetate form if 22.0 mL of 0.100 *M* $AgNO_3$ were added to 45.0 mL of 0.0260 *M* $NaC_2H_3O_2$? For $AgC_2H_3O_2$, $K_{sp} = 2.3 \times 10^{-3}$.

18.58 Suppose 50.0 mL each of 0.0100 *M* solutions of NaBr and $Pb(NO_3)_2$ are poured together. Does a precipitate form? If so, calculate the molar concentrations of the ions at equilibrium.

18.59 If a solution of 0.10 *M* Mn^{2+} and 0.10 *M* Cd^{2+} is gradually made basic, what will the concentration of Cd^{2+} be when $Mn(OH)_2$ just begins to precipitate? Assume no change in the volume of the solution.

Selective Precipitation

18.60 Both AgCl and AgI are very sparingly soluble salts, but the solubility of AgI is much less than that of AgCl, as can be seen by their K_{sp} values. Suppose that a solution contains both Cl^- and I^- with $[Cl^-] = 0.050$ *M* and $[I^-] = 0.050$ *M*. If solid $AgNO_3$ is added to 1.00 L of this mixture (so that no appreciable change in volume occurs), what is the value of $[I^-]$ when AgCl first begins to precipitate?

18.61 Suppose that Na_2SO_4 is added gradually to 100.0 mL of a solution that contains both Ca^{2+} ion (0.15 *M*) and Sr^{2+} ion (0.15 *M*). **(a)** What will the Sr^{2+} concentration be (in mol L^{-1}) when $CaSO_4$ just begins to precipitate? **(b)** What percentage of the strontium ion has precipitated when $CaSO_4$ just begins to precipitate?

ILW OH **18.62** What value of $[H^+]$ and what pH permits the selective precipitation of the sulfide of just one of the two metal ions in a solution that has a concentration of 0.010 *M* Pb^{2+} and 0.010 *M* Co^{2+}?

18.63 What pH would yield the maximum separation of Mn^{2+} from Sn^{2+} in a solution that is 0.010 *M* in Mn^{2+}, 0.010 *M* in Sn^{2+}, and saturated in H_2S? (Assume the green form of MnS in Table 18.2.)

18.64 What range of pH would permit the selective precipitation of Cu^{2+} as $Cu(OH)_2$ from a solution that contains 0.10 *M* Cu^{2+} and 0.10 *M* Mn^{2+}? For $Mn(OH)_2$, $K_{sp} = 1.6 \times 10^{-13}$, and for $Cu(OH)_2$, $K_{sp} = 4.8 \times 10^{-20}$.

18.65 Kidney stones often contain insoluble calcium oxalate, CaC_2O_4, which has a $K_{sp} = 2.3 \times 10^{-9}$. Calcium oxalate is considerably less soluble than magnesium oxalate, MgC_2O_4, which has a $K_{sp} = 4.8 \times 10^{-6}$. Suppose a solution contained both Ca^{2+} and Mg^{2+} at a concentration of 0.10 *M*. What pH would be required to achieve maximum separation of these ions by precipitation of CaC_2O_4 if the solution also contains oxalic acid, $H_2C_2O_4$ at a concentration of 0.10 *M*? For $H_2C_2O_4$, $K_{a_1} = 6.5 \times 10^{-2}$ and $K_{a_2} = 6.1 \times 10^{-5}$.

***18.66** A chemist has a solution containing Ag^+ and Ni^{2+} and would like to separate them by precipitating one of the metals by forming the carbonate of that metal. If carbon dioxide is bubbled into the solution to make a saturated $CO_2(aq)$ solution, approximately 0.030 *M*, in what pH range would it be possible to precipitate the silver ion as silver(I) carbonate and leave the nickel(II) ions in solution?

***18.67** In the metal plating industry, the waste is often contaminated with Zn^{2+} and Ni^{2+}. In order to save the metals, they are recovered by precipitating them as the carbonate salts. In what pH range would it be possible to separate and collect the zinc(II) ions and then the nickel(II) ions? The concentration of CO_2 is 0.030 *M*.

Complex Ion Equilibria

18.68 Write the chemical equilibria and equilibrium laws that correspond to K_{form} for the following complexes:

(a) $CuCl_4^{2-}$ **(b)** AgI_2^- **(c)** $Cr(NH_3)_6^{3+}$

18.69 Write the chemical equilibria and equilibrium laws that correspond to K_{form} for the following complexes:

(a) $Ag(S_2O_3)_2^{3-}$ **(b)** $Zn(NH_3)_4^{2+}$ **(c)** SnS_3^{2-}

OH 18.70 Write equilibria that correspond to K_{form} for each of the following complex ions and write the equations for K_{form}:

(a) $Co(NH_3)_6^{3+}$ **(b)** HgI_4^{2-} **(c)** $Fe(CN)_6^{4-}$

18.71 Write the equilibria that are associated with the equations for K_{form} for each of the following complex ions. Write also the equations for the K_{form} of each.

(a) $Hg(NH_3)_4^{2+}$ **(b)** SnF_6^{2-} **(c)** $Fe(CN)_6^{3-}$

18.72 Write equilibria that correspond to K_{inst} for each of the following complex ions and write the equations for K_{inst}:

(a) $Co(NH_3)_6^{3+}$ **(b)** HgI_4^{2-} **(c)** $Fe(CN)_6^{4-}$

18.73 Write the equilibria that are associated with the equations for K_{inst} for each of the following complex ions. Write also the equations for the K_{inst} of each.

(a) $Hg(NH_3)_4^{2+}$ **(b)** SnF_6^{2-} **(c)** $Fe(CN)_6^{3-}$

18.74 For $PbCl_3^-$, $K_{form} = 2.5 \times 10^1$. Use this information plus the K_{sp} for $PbCl_2$ to calculate K_c for the follwing reaction:

$$PbCl_2(s) + Cl^-(aq) \rightleftharpoons PbCl_3^-(aq)$$

18.75 The overall formation constant for $Ag(CN)_2^-$ equals 5.5×10^{18}, and the K_{sp} for AgCN equals 6.0×10^{-17}. Calculate K_c for the following reaction:

$$AgCN(s) + CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$$

18.76 How many grams of solid NaCN have to be added to 1.2 L of water to dissolve 0.11 mol of $Fe(OH)_3$ in the form of $Fe(CN)_6^{3-}$? Use data as needed from Tables 18.1 and 18.3. (For simplicity, ignore the reaction of CN^- ion with water.)

18.77 In photography, unexposed silver bromide is removed from film by soaking the film in a solution of sodium thiosulfate, $Na_2S_2O_3$. Silver ion forms a soluble complex with thiosulfate ion, $S_2O_3^{2-}$, which has the formula $Ag(S_2O_3)_2^{3-}$, and formation of the complex causes the AgBr in the film to dissolve. The $Ag(S_2O_3)_2^{3-}$complex has $K_{form} = 2.0 \times 10^{13}$. How many grams of AgBr ($K_{sp} = 5.4 \times 10^{-13}$) will dissolve in 125 mL of 1.20 *M* $Na_2S_2O_3$ solution?

18.78 Silver iodide is very insoluble and can be difficult to remove from glass apparatus, but it forms a relatively stable complex ion, AgI_2^- ($K_{form} = 1 \times 10^{11}$), that makes AgI fairly soluble in a solution containing I^-. When a solution containing the AgI_2^- ion is diluted with water, AgI precipitates. Explain why this happens in terms of the equilibria that are involved. How many grams of AgI will dissolve in 0.100 L of 1.0 *M* KI solution?

18.79 Silver forms a sparingly soluble iodide salt, AgI, and it also forms a soluble iodide complex, AgI_2^- ($K_{form} = 1 \times 10^{11}$). How many grams of potassium iodide must be added to 0.100 L of water to dissolve 0.020 mol of AgI? (*Hint*: Be sure to include *all* of the iodide that's added to the solution.)

18.80 The formation constant for $Ag(CN)_2^-$ equals 5.3×10^{18}. Use the data in Table 18.1 to determine the molar solubility of AgI in 0.010 *M* KCN solution.

18.81 Suppose that some dipositive cation, M^{2+}, is able to form a complex ion with a ligand, *L*, by the following balanced equation:

$$M^{2+} + 2L \rightleftharpoons M(L)_2^{2+}$$

The cation also forms a sparingly soluble salt, MCl_2. In which of the following circumstances would a given quantity of ligand be more able to bring larger quantities of the salt into solution? Explain and justify the calculation involved.

(a) $K_{form} = 1 \times 10^2$ and $K_{sp} = 1 \times 10^{-15}$

(b) $K_{form} = 1 \times 10^{10}$ and $K_{sp} = 1 \times 10^{-20}$

18.82 The molar solubility of $Zn(OH)_2$ in 1.0 *M* NH_3 is 5.7×10^{-3} mol L^{-1}. Determine the value of the instability constant of the complex ion, $Zn(NH_3)_4^{2+}$. Ignore the reaction, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.

OH 18.83 Calculate the molar solubility of $Cu(OH)_2$ in 2.0 *M* NH_3. (For simplicity, ignore the reaction of NH_3 as a base.)

Additional Exercises

*18.84 What ratio of K_{sp} values will allow for the use of selective precipitation to separate two ionic compounds in which the less soluble one has less than 0.01% remaining when the more soluble one begins to precipitate? To make the calculation easier, assume that both compounds have one-to-one ratios of cation to anion.

*18.85 A student had a solution that contained Pb^{2+}, Ni^{2+}, and Cd^{2+} and wanted to separate the ions. The student added H_2S and acidified the solution to pH 0.5. The precipitate was collected and then the student raised the pH to 8.0 and another solid precipitated. Finally, the student added HCl, expecting to collect lead(II) chloride. Was the student able to collect the $PbCl_2$? What was in the first and second precipitates?

18.86 Magnesium hydroxide, $Mg(OH)_2$, found in milk of magnesia, has a solubility of 7.05×10^{-3} g L^{-1} at 25 °C. Calculate K_{sp} for $Mg(OH)_2$.

18.87 Does iron(II) sulfide dissolve in 8 *M* HCl? Perform the calculations that prove your answer.

18.88 In an aqueous suspension of $Ca(OH)_2$, the only other component is water. Use K_{sp} to estimate the pH of the suspension.

*18.89 Suppose that 25.0 mL of 0.10 *M* HCl is added to 1.000 L of saturated $Mg(OH)_2$ in contact with more than enough $Mg(OH)_2(s)$ to react with all of the HCl. After reaction has ceased, what will the molar concentration of Mg^{2+} be? What will the pH of the solution be?

OH *18.90 Solid $Mn(OH)_2$ is added to a solution of 0.100 *M* $FeCl_2$. After reaction, what will be the molar concentrations of Mn^{2+} and Fe^{2+} in the solution? What will be the pH of the solution? For $Mn(OH)_2$, $K_{sp} = 1.6 \times 10^{-13}$.

*18.91 Suppose that 50.0 mL of 0.12 *M* $AgNO_3$ is added to 50.0 mL of 0.048 *M* NaCl solution. **(a)** What mass of AgCl will form? **(b)** Calculate the final concentrations of all of the ions in the solution that is in contact with the precipitate. **(c)** What percentage of the Ag^+ ions have precipitated?

*18.92 A sample of hard water was found to have 278 ppm Ca^{2+} ion. Into 1.00 L of this water, 1.00 g of Na_2CO_3 was dissolved. What is the new concentration of Ca^{2+} in parts per million? (Assume that the addition of Na_2CO_3 does not change the volume, and assume that the density of the aqueous solutions involved are all 1.00 g mL^{-1}.)

*18.93 What value of $[H^+]$ and what pH would allow the selective separation of the carbonate of just one of the two metal ions in a solution that has a concentration of 0.010 *M* La^{3+} and 0.010 *M* Pb^{2+}? For $La_2(CO_3)_3$, $K_{sp} = 4.0 \times 10^{-34}$; for $PbCO_3$, $K_{sp} = 7.4 \times 10^{-14}$. A saturated solution of CO_2 in water has a concentration of H_2CO_3 equal to 3.3×10^{-2} *M*.

*18.94 When solid NH_4Cl is added to a suspension of $Mg(OH)_2(s)$, some of the $Mg(OH)_2$ dissolves.

(a) Write equations for *all* of the chemical equilibria that exist in the solution after the addition of the NH_4Cl.

(b) How many moles of NH_4Cl must be added to 1.0 L of a suspension of $Mg(OH)_2$ to dissolve 0.10 mol of $Mg(OH)_2$?

(c) What is the pH of the solution after the 0.10 mol of $Mg(OH)_2$ has dissolved in the solution containing the NH_4Cl?

*18.95 After solid $CaCO_3$ was added to a slightly basic solution, the pH was measured to be 8.50. What was the molar solubility of $CaCO_3$ in this solution?

18.96 What is the molar solubility of $Fe(OH)_3$ in water? (*Hint*: You have to take into account the self-ionization of water.)

*18.97 In Example 18.11 (page 860) we say, “there are relatively few uncomplexed Ag^+ ions in the solution.” Calculate the molar concentration of Ag^+ ion actually left after the complex forms as described in Example 18.11.

*18.98 What are the concentrations of Pb^{2+}, Br^-, and I^- in an aqueous solution that’s in contact with both PbI_2 and $PbBr_2$?

*18.99 Will a precipitate form in a solution made by dissolving 1.0 mol of $AgNO_3$ and 1.0 mol $HC_2H_3O_2$ in 1.0 L of solution? For $AgC_2H_3O_2$, $K_{sp} = 2.3 \times 10^{-3}$, and for $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$.

*18.100 How many grams of solid sodium acetate must be added to 0.200 L of a solution containing 0.200 *M* $AgNO_3$ and 0.10 *M* nitric acid to cause silver acetate to begin to precipitate? For $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$, and for $AgC_2H_3O_2$, $K_{sp} = 2.3 \times 10^{-3}$.

*18.101 How many grams of solid potassium fluoride must be added to 200 mL of a solution that contains 0.20 *M* $AgNO_3$ and 0.10 *M* acetic acid to cause silver acetate to begin to precipitate? For HF, $K_a = 6.5 \times 10^{-4}$; for $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$; and for $AgC_2H_3O_2$, $K_{sp} = 2.3 \times 10^{-3}$.

*18.102 What is the molar solubility of $Mg(OH)_2$ in 0.10 *M* NH_3 solution? Remember that NH_3 is a weak base.

*18.103 If 100 mL of 2.0 *M* NH_3 is added to 0.400 L of a solution containing 0.10 *M* Mn^{2+} and 0.10 *M* Sn^{2+}, what minimum number of grams of HCl would have to be added to the mixture to prevent $Mn(OH)_2$ from precipitating? For $Mn(OH)_2$, $K_{sp} = 1.6 \times 10^{-13}$. Assume that virtually all of the tin is precipitated as $Sn(OH)_2$ by the following reaction:

$$Sn^{2+}(aq) + 2NH_3(aq) + 2H_2O \longrightarrow Sn(OH)_2(s) + 2NH_4^+(aq)$$

***18.104** What is the molar concentration of Cu^{2+} ion in a solution prepared by mixing 0.50 mol of NH_3 and 0.050 mol of $CuSO_4$ in 1.00 L of solution? For NH_3, $K_b = 1.8 \times 10^{-5}$; for $Cu(OH)_2$, $K_{sp} = 4.8 \times 10^{-20}$; and for $Cu(NH_3)_4{}^{2+}$, $K_{form} = 4.8 \times 10^{12}$.

***18.105** On the basis of the K_{sp} of $Al(OH)_3$, what would be the pH of a mixture consisting of solid $Al(OH)_3$ mixed with pure water? (Assume 100% dissociation of the aluminum hydroxide.)

***18.106** The compound EDTA is used to remove soap scum, as it was described in the *Chemistry Outside the Classroom 18.1.* It has also been used to treat heavy metal poisoning, especially lead and mercury poisoning. The reaction of lead with EDTA is

$$Pb^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons PbEDTA^{2-}(aq) \qquad K = 1.1 \times 10^{18}$$

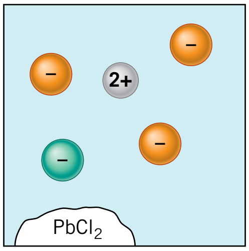
If a 1.0 L solution of 0.15 M $Pb(NO_3)_2$ containing 0.10 M $EDTA^{-4}$ is at a pH of 12.50, will $Pb(OH)_2$ precipitate?

***18.107** A chemist has a solution that contains a mixture of the following metal ions: Cu^{2+}, Co^{2+}, Ba^{2+}, Pb^{2+}, Ag^+, Mn^{2+}, Ca^{2+}, and Bi^{3+}. How can these ions be separated? Can all of them be separated? Which ones cannot be separated from each other?

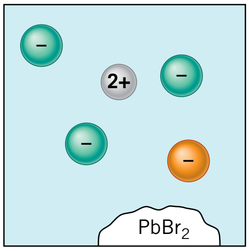
18.108 You are given a sample containing NaCl(aq) and NaBr(aq), both with concentrations of 0.020 M. Some of the figures at the right represent a series of snapshots of what molecular-level views of the sample would show as a 0.200 M $Pb(NO_3)_2(aq)$ solution is slowly added. In these figures, Br^- is red-brown, and Cl^- is green. Also, spectator ions are not shown, nor are ions whose concentrations are much less than the other ions. The K_{sp} constants for $PbCl_2$ and $PbBr_2$ are 1.7×10^{-5} and 6.6×10^{-6}, respectively.

(1) Arrange the figures in a time sequence to show what happens as the lead(II) nitrate solution is added, excluding any that do not "make sense."

(2) Explain why you excluded any figures that did not belong in the observed time sequence.



(a)



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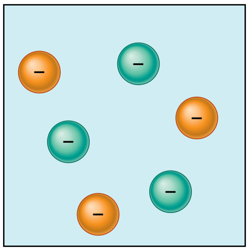

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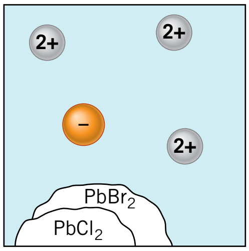

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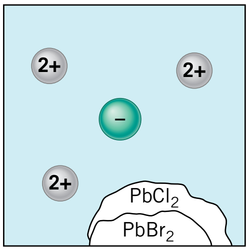


(e)

Multi-Concept Problems

***18.109** What is the age of a stalagmite, if it has accumulated from a saturated $CaCO_3$ solution dropping at a rate of 1 drop per second? The stalagmite is a cone 10 ft in diameter and 16 ft high. The density of $CaCO_3$ is 2.71 g cm^{-3}. Assume that there are 10 drops of water in one milliliter of water and that the water evaporates when it hits the stalagmite.

***18.110** In modern construction, walls and ceilings are constructed of "drywall," which consists of plaster sandwiched between sheets of heavy paper. Plaster is composed of calcium sulfate, $CaSO_4 \cdot 2H_2O$. Suppose you had a leak in a water pipe that was dripping water on a drywall ceiling 1/2 in. thick at a rate of 2.00 L per day. Use the K_{sp} of calcium sulfate to estimate how many days it would take to dissolve a hole 1.0 cm in diameter. Assume the density of the plaster is 0.97 g cm^{-3}.

***18.111** How many milliliters of 0.10 M HCl would have to be added to 100 mL of a saturated solution of $PbCl_2$ in contact with 50.0 g of solid $PbCl_2$ to reduce the Pb^{2+} concentration to 0.0050 M?

***18.112** Marble is composed primarily of $CaCO_3$, a slightly soluble salt. Unfortunately, it is attacked by the acid in acid rain. What is the solubility of $CaCO_3$ in rain water (pH = 5.6) and acid rain (pH = 4.20)?

***18.113** The pH of a saturated solution of $Mg(OH)_2$ is 9.8. Determine the K_{sp} for $Mg(OH)_2$.

***18.114** The osmotic pressure of a saturated solution of $NiCO_3$ is 13 torr at 25 °C. From this information, calculate the K_{sp} for $NiCO_3$. Ignore the reaction of the carbonate ion with water.

Exercises in Critical Thinking

18.115 Consider mercury(II) sulfide, HgS, which has a solubility product of 2×10^{-53}. Suppose some solid HgS was added to 1.0 L of water. How many ions of Hg^{2+} and S^{2-} are present in the water when equilibrium is reached? If your answer is accurate, is there a true equilibrium between HgS(*s*) and the ions in the solution? Explain your answer.

18.116 If aqueous ammonia is added gradually to a solution of copper sulfate, a pale blue precipitate forms that then dissolves to give a deep blue solution. Describe the chemical reactions that take place during these changes.

18.117 From a practical standpoint, can you effectively separate Pb^{2+} and Sr^{2+} ions by selective precipitation of their sulfates? Support your conclusions using calculations.

18.118 A salt with the formula of MX_2, and a molar mass of approximately 200, is slightly soluble in water. Estimate the minimum reliable mass you can determine on your laboratory balance. Use that estimate to determine the smallest value of the solubility product of MX_2 that could be determined by evaporating a liter of a solution that is saturated in MX_2.

18.119 In older textbooks, the solubility equilibrium for lead(II) sulfide was written as $PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$, with $K_{sp} = 3 \times 10^{-28}$. Calculate the solubility of lead(II) sulfide using K_{sp} (assuming no reaction of S^{2-} with water) and with K_{spa}. Is there a difference between the two answers? Discuss the results of your calculations.

18.120 Suppose two silver wires, one coated with silver chloride and the other coated with silver bromide, are placed in a beaker containing pure water. Over time, what if anything will happen to the compositions of the coatings on the two wires? Justify your answer.

19 Thermodynamics

Chapter Outline

19.1 | First Law of Thermodynamics

19.2 | Spontaneous Change

19.3 | Entropy

19.4 | Second Law of Thermodynamics

19.5 | Third Law of Thermodynamics

19.6 | Standard Free Energy Change, $\Delta G°$

19.7 | Maximum Work and ΔG

19.8 | Free Energy and Equilibrium

19.9 | Equilibrium Constants and $\Delta G°$

19.10 | Bond Energies

Invented at Bell Laboratories in 1945, the drinking toy bird in this photo will suddenly tilt itself forward until its beak dips into a glass of water. When it apparently satisfies its thirst, it tilts back to an erect position. Soon it gets "thirsty" again and repeats the process, seemingly endlessly. In the cycle, the drinking bird absorbs water into the felt material on its head. The water, which is relatively warm, causes the dichloromethane, CH_2Cl_2, liquid inside the bird to evaporate slightly, pushing liquid toward the tail. When enough dichloromethane reaches the tail, the bird "stands up." When the bird is in the erect position the water evaporates from the felt head, causing some of the dichloromethane to condense. This creates a slight vacuum that draws liquid toward the head, and the bird dips down for another drink. Our bird is an example of a thermodynamic cycle (actually a heat engine) and the motions that can be generated by the flow of heat. Chapter 7 taught us about heat energy, and Chapters 11 and 12 taught the properties of gases and phase changes. This chapter brings many of these ideas together and extends them to consider criteria for spontaneous reactions, chemical equilibrium, and work that can be extracted from chemical reactions. (Corbis/SuperStock)

This Chapter in Context

The chemistry we observe in our world is controlled both by what *can* happen and what *cannot*. For example, hydrocarbon fuels such as octane (C_8H_{18}) *can* burn, forming CO_2 and H_2O and releasing heat. When combustion reactions are started, they proceed *spontaneously* (i.e., on their own, without further assistance), and we use them to provide energy to move vehicles, generate electricity, and heat homes and offices. On the other hand, if we mix CO_2 and H_2O, there is nothing we can do to entice them to react spontaneously to form hydrocarbons. These reactions *cannot* take place on their own. If they could, our problems with fossil fuel supplies and greenhouse gas production could easily be solved.

Observations like those described above raise the fundamental question, What determines whether or not a chemical reaction is possible when substances are combined? The answer to this question is found in the study of thermodynamics, which expands on topics introduced in Chapter 7—energy and chemical change. As you will see, not only will we be able to use thermodynamics to determine the possibility of reaction, but also we will find another explanation of chemical equilibrium and another way of determining numerical values for equilibrium constants.

19.1 | First Law of Thermodynamics

■ *Thermo* implies heat, *dynamics* implies movement.

Chemical thermodynamics is the study of the role of energy in chemical changes and in determining the behavior of materials. It is based on a few laws that summarize centuries of experimental observation. Each law is a statement about relationships between energy, heat, work, and temperature. Because the laws manifest themselves in so many different ways and underlie so many different phenomena, there are many alternative but equivalent ways to state them. For ease of reference, the laws are identified by number and are called the first law, the second law, and the third law of thermodynamics.

The **first law of thermodynamics**, which was discussed in Chapter 7, states that internal energy may be transferred as heat or work but it cannot be created or destroyed. This law, you recall, serves as the foundation for Hess's law, which we used in our computations involving enthalpy changes in Chapter 7. Let's review the first law in more detail.

Recall that the **internal energy** of a system, which is given the symbol E, is the system's total energy—the sum of all the kinetic and potential energies of its particles. For a chemical reaction, a change in the internal energy, ΔE, is defined as

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

Thus, ΔE is positive if energy flows into a system and negative if energy flows out.

The first law of thermodynamics considers two ways by which energy can be exchanged between a system and its surroundings. One is by the absorption or release of heat, which is given the symbol q. The other involves work, w. If *work is done on a system*, as in the compression of a gas, the system gains and stores energy. Conversely, if *the system does work on the surroundings*, as when a gas expands and pushes a piston, the system loses some energy by changing part of its potential energy to kinetic energy, which is transferred to the surroundings. The **first law of thermodynamics** expresses the net change in energy mathematically by the equation

■ ΔE = (heat input) + (work input)

$$\Delta E = q + w$$

In Chapter 7 you learned that a positive sign on an energy change indicates energy gained by the system, whereas a negative sign indicates energy lost by the system. Thus, when . . .

q is (+)	Heat is absorbed by the system.
q is (−)	Heat is released by the system.
w is (+)	Work is done on the system.
w is (−)	Work is done by the system.

In the lab you may observe the reaction beaker becoming cool if q has a positive sign and you may feel it warm when heat is released. Similarly, you might observe the system expanding, especially when a gas is evolved, when work has a negative sign.

In Chapter 7 you also learned that ΔE is the difference between two state functions, $E_{\text{final}} - E_{\text{initial}}$, which means that its value does not depend on how a change from one state to another is carried out. The values of q and w strongly depend on how the system changes, as we illustrated in Figure 7.8 on page 270, and are not state functions. Engineers often try to maximize the work obtained for a given change while minimizing the loss of energy in the form of heat. The ratio of $w/\Delta E$ is called the thermodynamic efficiency of a given process.

Figure 19.1 | **Expanding gases can do work.** In a steam engine, such as the one powering this locomotive, heat is absorbed by water to turn it into high temperature, high pressure steam (q is positive). The steam then expands, pushing pistons and causing the locomotive to move. In the expansion, the steam does work and w is negative. *(Richard A. CookeIII/Stone/Getty Images)*

Pressure–Volume Work

There are two kinds of work that chemical systems can do (or have done on them) that are of concern to us. One is electrical work, which is examined in Chapter 20 and will be discussed there. The other is work associated with the expansion or contraction of a system under the influence of an external pressure. An example is the work you perform on a gas when you compress it to fill a tire (Figure 19.2). Such "pressure–volume" or P–V work was discussed in Chapter 7, where it was shown that this kind of work is given by the equation

$$w = -P\,\Delta V$$

where P is the *external pressure* on the system.

If P–V work, similar to the work that powers the diesel engine in Figure 19.3, is the only kind of work involved in a chemical change, the equation for ΔE takes the form

$$\Delta E = q + (-P\,\Delta V) = q - P\,\Delta V$$

In Chapter 7, we also showed that when a reaction takes place in a container whose volume cannot change, the entire energy change must appear as heat. Therefore, ΔE is called the heat at constant volume (q_v)

$$\Delta E = q_v$$

Figure 19.2 | **Work being done on a gas.** When a gas is *compressed* by an external pressure, w is positive because work is done on the gas. Because V decreases when the gas is compressed, the negative sign assures that w will be positive for the compression of a gas. *(Lawrence Manning/Corbis Images)*

Figure 19.3 | **Diesel engines are highly efficient.** In the cylinders of a diesel engine, air becomes very hot when compressed to a small volume because the work energy of compression is converted into heat energy. The temperature is so high that the fuel ignites when injected into the cylinder. The small explosion that occurs pushes the pistons to power large trucks and heavy equipment such as this diesel locomotive. *(John Griffin/The Image Works)*

Practice Exercises

19.1 | Molecules of an ideal gas have no intermolecular attractions and, therefore, undergo no change in potential energy on expansion of the gas. If the expansion is also at a constant temperature, there is no change in the kinetic energy, so the **isothermal** (constant temperature) expansion of an ideal gas has $\Delta E = 0$. Suppose such a gas expands at constant temperature from a volume of 1.0 L to 12.0 L against a constant opposing pressure of 14.0 atm. In units of *L atm*, what are q and w for this change? (*Hints*: Is the system doing work, or is work done on the system? What must be the sum of q and w in this case?)

19.2 | If a gas is compressed under **adiabatic** conditions (allowing no transfer of heat to or from the surroundings) by application of an external pressure, the temperature of the gas increases. Why?

Enthalpy

Rarely do we carry out reactions in containers of fixed volume. Usually, reactions take place in containers open to the atmosphere where they are exposed to a constant pressure. To study heats of reactions under constant pressure conditions, the term enthalpy is used. Recall that the **enthalpy, *H*,** is defined by the equation

$$H = E + PV$$

In Section 7.5 we showed that at constant pressure, the **enthalpy change, Δ*H*,** is equal to q_p

$$\Delta H = q_p$$

where q_p is the **heat at constant pressure**.

The Difference between ΔE and ΔH

In Chapter 7 we noted that ΔE and ΔH are not equal. They differ by the pressure–volume work, $-P\,\Delta V$.

$$\Delta E - \Delta H = -P\,\Delta V$$

■ The ΔV values for reactions involving only solids and liquids are very tiny, so ΔE and ΔH for these reactions are nearly the same size.

The only time ΔE and ΔH differ by a significant amount is when gases are formed or consumed in a reaction, and even then they do not differ by much. To calculate ΔE from ΔH (or ΔH from ΔE), we must have a way of calculating the pressure–volume work.

If we assume the gases in the reaction behave as ideal gases, then we can use the ideal gas law, rearranged to solve for V:

$$V = \frac{nRT}{P}$$

A volume change can therefore be expressed as

$$\Delta V = \Delta\left(\frac{nRT}{P}\right)$$

If pressure and temperature are held constant, only n can vary. We show this as Δn and write

$$\Delta V = \Delta n\left(\frac{RT}{P}\right)$$

Thus, when the reaction occurs at constant pressure, the volume change is caused by a change in the number of moles of *gas*. Of course, in chemical reactions not all reactants and products need to be gases, so to be sure we compute Δn correctly, let's express the change in the number of moles of gas as Δn_{gas}. It's defined as

$$\Delta n_{gas} = (n_{gas})_{products} - (n_{gas})_{reactants}$$

The $P\Delta V$ product is therefore,

$$P\Delta V = P \cdot \Delta n_{\text{gas}}\left(\frac{RT}{P}\right) = \Delta n_{\text{gas}} RT$$

Substituting into the equation for ΔH gives

$$\Delta H = \Delta E + \Delta n_{\text{gas}} RT \tag{19.1}$$

TOOLS

Converting between ΔE and ΔH

The following example illustrates how small the difference is between ΔE and ΔH.

Example 19.1
Conversion between ΔE and ΔH

The decomposition of calcium carbonate in limestone is used industrially to make lime, CaO, for manufacturing cement.

$$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$$

The reaction is endothermic and has $\Delta H° = +571$ kJ. What is the value of $\Delta E°$ for this reaction, and what is the difference between $\Delta H°$ and $\Delta E°$?

Analysis: In the preceding section we were reminded that the difference between the internal energy and the enthalpy is $-P\Delta V$. When temperature and pressure are held constant, $-P\Delta V$ is equal to $-\Delta n_{\text{gas}} RT$. Finally, the system is at standard state, as indicated by the superscript °, so the temperature is 25 °C; the number of moles can be obtained from the coefficients in the balanced chemical equation.

Assembling the Tools: We need to use the balanced chemical equation given in the problem statement and Equation 19.1.

$$\Delta H = \Delta E + \Delta n_{\text{gas}} RT$$

We add the superscript ° to ΔH and ΔE, and that defines a temperature of 25 °C (standard temperature for measuring heats of reaction). It is also important to remember that in calculating Δn_{gas}, we count just the moles of gas. Also, because we wish to calculate the term nRT in units of kilojoules, we will use $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, being sure to convert J to kJ at the appropriate time.

Solution: Solving for ΔE and applying the superscript ° gives

$$\Delta E° = \Delta H° - \Delta n_{\text{gas}} RT$$

To calculate Δn_{gas} our chemical equation shows that there is one mole of gas among the products and no moles of gas among the reactants, so

$$\Delta n_{\text{gas}} = 1 \text{ mol} - 0 \text{ mol} = 1 \text{ mol}$$

The temperature is 298 K, and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Substituting,

$$\begin{aligned} \Delta E° &= +571 \text{ kJ} - (1 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \\ &= +571 \text{ kJ} - 2480 \text{ J} \end{aligned}$$

We cannot add units of kJ to units of J, so we convert 2480 J to 2.48 kJ

$$\begin{aligned} \Delta E° &= +571 \text{ kJ} - 2.48 \text{ kJ} \\ &= +569 \text{ kJ} \end{aligned}$$

The difference between $\Delta H°$ and $\Delta E°$ is $\Delta n_{\text{gas}} RT$, or 2.48 kJ.

Is the Answer Reasonable? The equation we used predicts that $\Delta E°$ should be smaller than $\Delta H°$ if there is an increase in the moles of gas. Our result agrees with that assessment. We found the difference to be relatively small, which also agrees with the text above. Finally, the energy needed to decompose CaCO_3 at constant volume ($\Delta E°$) should be less than the energy needed at constant pressure ($\Delta H°$), because the enthalpy includes additional energy to do the work of pushing back the atmosphere as the system expands.

Practice Exercises

19.3 | Calculate the difference, in kilojoules, between ΔE and ΔH for the following exothermic reaction at 45 °C. Which is more exothermic, ΔE or ΔH? (*Hint*: Note the temperature.)

$$2N_2O(g) + 3O_2(g) \longrightarrow 4NO_2(g)$$

19.4 | The reaction

$$CaO(s) + 2HCl(g) \longrightarrow CaCl_2(s) + H_2O(g)$$

has $\Delta H° = -217.1$ kJ. Calculate $\Delta E°$ for this reaction. What is the percentage difference between $\Delta E°$ and $\Delta H°$? (Use one significant figure for your percentage.)

When we examine the result of Example 19.1 we find that the difference between $\Delta E°$ and $\Delta H°$ is very small. In this case it works out to be approximately 0.5%.

19.2 | Spontaneous Change

Now that we've reviewed the way thermodynamics treats energy changes, we turn our attention to one of our main goals in studying this subject—finding relationships among the factors that determine whether or not a change in a system will occur spontaneously. By **spontaneous change** we mean one that occurs by itself, without continuous outside assistance. Examples are water flowing over a waterfall, the burning of natural gas on a stove, and the melting of ice cubes in a cold drink on a warm day. These are events that proceed on their own.

Some spontaneous changes occur very rapidly. An example is the detonation of a stick of dynamite, or the exposure of photographic film. Other spontaneous events, such as the rusting of iron or the erosion of stone, occur slowly, and many years may pass before a change is noticed. Still others occur at such an extremely slow rate under ordinary conditions that they appear not to be spontaneous at all. Gasoline–oxygen mixtures appear perfectly stable indefinitely at room temperature because under these conditions they react very slowly. However, if exposed to a spark, their rate of reaction increases tremendously and they react explosively.

Each day we also witness events that are obviously *not* spontaneous. We may pass by a pile of bricks in the morning and later in the day find that they have become a brick wall. We know from experience that the wall didn't get there by itself. A pile of bricks becoming a brick wall is *not* spontaneous; it requires the intervention of a bricklayer. Similarly, the decomposition of water into hydrogen and oxygen is not spontaneous. We see water all the time and we know that it's stable. Nevertheless, we can cause water to decompose by passing an electric current through it in a process called *electrolysis* (Figure 19.4).

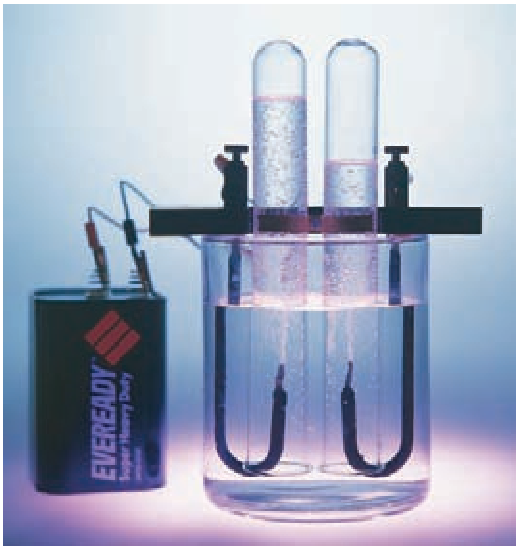


Figure 19.4 | **The electrolysis of water produces H_2 and O_2 gases.** It is a nonspontaneous change that only continues as long as electricity is supplied. *(Charles D. Winters/Photo Researchers)*

$$2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$

This decomposition will continue, however, only as long as the electric current is maintained. As soon as the supply of electricity is cut off, the decomposition ceases. This example demonstrates the difference between spontaneous and nonspontaneous changes. Once a spontaneous event begins, it has a tendency to continue until it is finished. A nonspontaneous event, on the other hand, can continue only as long as it receives some sort of outside assistance.

Nonspontaneous changes have another common characteristic. They are able to occur only when accompanied by some spontaneous change. For example, a bricklayer consumes food, and a series of spontaneous biochemical reactions then occur that supply the necessary muscle power to build the brick wall. Similarly, the nonspontaneous electrolysis of water requires some sort of spontaneous mechanical or chemical change to generate the needed electricity. In short, *all nonspontaneous events occur at the expense of spontaneous ones.* Everything that happens can be traced, either directly or indirectly, to spontaneous changes.

■ The driving of nonspontaneous reactions to completion by linking them to spontaneous ones is an important principle in biochemistry.

The reaction of gasoline vapor with oxygen, mentioned previously, illustrates an important observation about spontaneous changes. Even though the reaction between these substances has a strong tendency to occur, and is therefore spontaneous, the *rate of the reaction* at room temperature is so slow that the mixture appears to be stable. In other words, the reaction *appears* to be nonspontaneous because its rate is so slow. There are many reactions in nature that are spontaneous but occur at such a slow rate that they aren't observed. Biochemical reactions often fall into this category. Without the presence of a catalyst, an enzyme for instance, these reactions are so slow that effectively they do not occur. Living systems control their chemical reactions by selectively making enzymes available when spontaneous reactions or their products are needed.

Direction of Spontaneous Change

What determines the direction of spontaneous change? Let's begin by examining some everyday events such as those depicted in Figure 19.5. When iron rusts, heat is released, so the reaction lowers the internal energy of the system. Similarly, the chemical substances in the gasoline–oxygen mixture lose chemical energy by evolving heat as the gasoline burns to produce CO_2 and H_2O.

Since many spontaneous reactions are obviously exothermic, we might be tempted to conclude (as some nineteenth century chemists did) that spontaneous events occur because heat energy flows out of a system. This energy-lowering was labeled a "driving force" behind spontaneous change. In addition to the loss of heat energy in chemical reactions a change in potential energy can occur. For instance, when we drop a book, it spontaneously falls to the floor because that lowers its potential energy. Since a change that lowers the potential energy of a system is also exothermic, the old concept of spontaneity could be stated as: *Exothermic changes have a tendency to proceed spontaneously.*

■ Most, but not all, chemical reactions that are exothermic occur spontaneously.

Yet if this is so, how do we explain the third photograph in Figure 19.5? The melting of ice at room temperature is clearly a spontaneous process. But ice absorbs heat energy from the surroundings as it melts. This absorbed heat gives the water from the melted ice

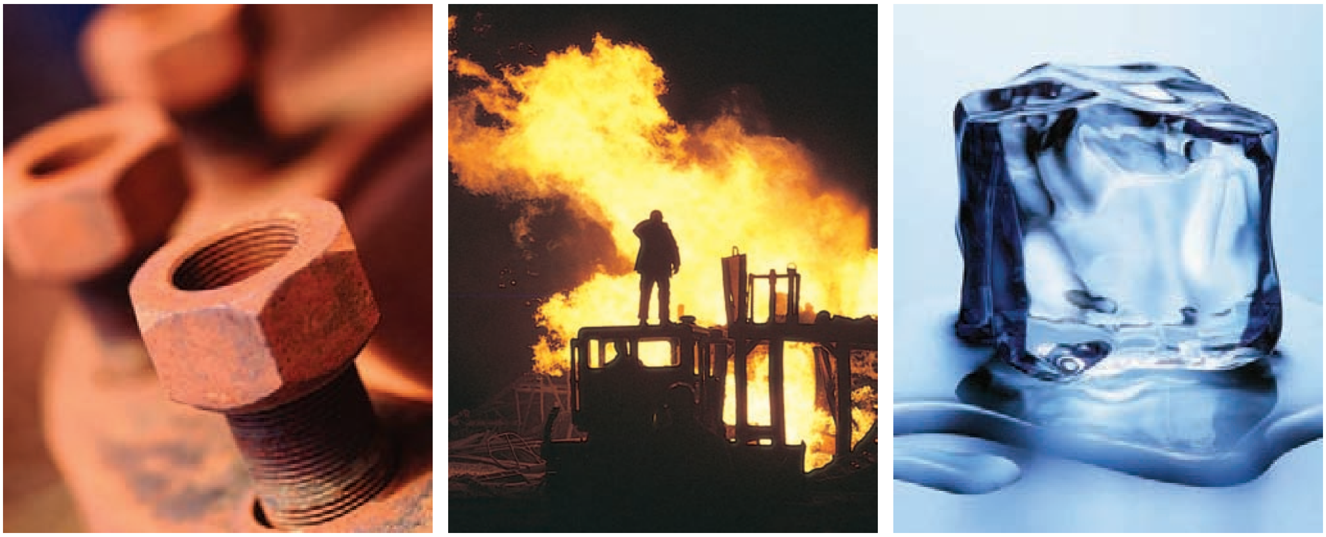


Figure 19.5 | **Three common spontaneous events.** Iron rusts, fuel burns, and an ice cube melts at room temperature. *(left) George B. Diebold/Corbis Images; (center) Lowell J. Georgia/Photo Researchers; (right) Daniel Smith/Corbis)*

cube a higher internal energy than the original ice had. This is an example of a spontaneous but endothermic process. There are many other examples of spontaneous endothermic processes: the evaporation of acetone in nail polish remover, the expansion of carbon dioxide gas into a vacuum, the reaction of acetic acid with sodium carbonate, and the operation of a chemical "cold pack."

In Chapter 13 we discussed the solution process, and we said that one of the principal driving forces in the formation of a solution is the fact that the mixed state is much more probable than the unmixed state. It turns out that arguments like this can be used to explain the direction of any spontaneous process.

19.3 | Entropy

In Chapter 7 you learned that when a hot object is placed in contact with a colder one, heat will flow spontaneously from the hot object to the colder one. But why? The law of conservation of energy doesn't help, since energy is conserved no matter in which direction the heat flows.

To analyze what happens in the spontaneous flow of heat, let's imagine a situation in which we have two objects in contact with one another, one with a high temperature and the other with a low temperature. Because of the relationship between average kinetic energy and temperature, we expect the high-temperature object to have many rapidly moving molecules, whereas the low-temperature object will have more slow-speed molecules. Where the objects touch, many of the molecular collisions will involve fast-moving "hot" molecules and slow-moving "cold" ones. In such a collision, it is very unlikely that the fast molecule will gain kinetic energy at the expense of the slow one. Instead, the fast molecule will lose kinetic energy and slow down, while the slow molecule will gain kinetic energy and speed up. Over time, the result of many such collisions is that the hot object cools and the cool object warms. While this happens, the combined kinetic energy of the two objects becomes distributed over all the molecules in the system.

■ Imagine a game of billiards where a moving ball, the cue ball, hits a stationary ball. In the collision, we observe that the cue ball loses some, but not all, of its speed and the other ball is now in motion. The result is the transfer of energy from the "hot" cue ball to the "cold" stationary ball.

What we learn here is that heat flows because of the probable outcome of intermolecular collisions. Viewed on a larger scale, the uniform distribution of kinetic energy between the objects, caused by the flow of heat, is much more probable than a situation in which no heat flow occurs, which illustrates the role of probability in determining the direction of a spontaneous change. *Spontaneous processes tend to proceed from states of low probability to states of higher probability.* The higher probability states are those that allow more options for distributing energy among the molecules, so we can also say that *spontaneous processes tend to disperse energy.*

Distributing Energy in a System

■ The greater the statistical probability of a particular state, the greater is the entropy.

Because statistical probability is so important in determining the outcome of chemical and physical events, thermodynamics defines a state function, called **entropy** (symbol ***S***), that is related to the possible number of equivalent ways that energy can be distributed in a system. The greater the number of ways to distribute energy, the larger is its statistical probability, and therefore the larger the value of the entropy (Figure 19.6). Figure 19.7 represents another way to visualize the spreading of energy, this time in the form of monetary units, into equivalent states.

Because entropy is a state function, a change in entropy, ΔS, is independent of the path taken between initial and final states. Therefore, we can write

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

For a chemical reaction this becomes

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

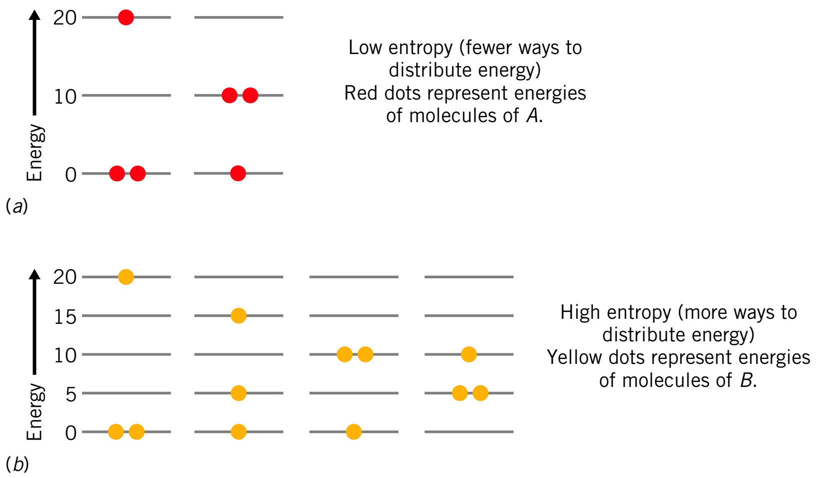

Energy
20
10
0
Low entropy (fewer ways to distribute energy)
Red dots represent energies of molecules of *A*.
(*a*)
Energy
20
15
10
5
0
High entropy (more ways to distribute energy)
Yellow dots represent energies of molecules of *B*.
(*b*)

Figure 19.6 | **A positive value for ΔS means an increase in the number of ways energy can be distributed among a system's molecules.** Consider the reaction $A \longrightarrow B$, where *A* can take on energies that are multiples of 10 energy units, and *B* can take on energies that are multiples of five units. Suppose that the total energy of the reacting mixture is 20 units. (*a*) There are two ways to distribute 20 units of energy among three molecules of *A*. (*b*) There are four ways to distribute 20 units of energy among three molecules of *B*. The entropy of *B* is higher than the entropy of *A* because there are more ways to distribute the same amount of energy in *B* than in *A*.

As you can see, when S_{final} is larger than S_{initial} (or when S_{products} is larger than $S_{\text{reactants}}$), the value of ΔS is positive. A positive value for ΔS means an increase in the number of energy-equivalent ways the system can be arranged, and we have seen that this kind of change tends to be spontaneous. This leads to a general statement about entropy:

> Any event that is accompanied by an increase in the entropy of the system will have a *tendency* to occur spontaneously.

Factors that Affect ΔS

It is often possible to predict whether ΔS is positive or negative for a particular change. This is because several factors influence the magnitude of the entropy in predictable ways.

Volume

For gases, the entropy increases with increasing volume, as illustrated in Figure 19.8. At the left we see a gas confined to one side of a container, separated from a vacuum by a removable partition. Let's suppose the partition could be pulled away in an instant, as shown in Figure 19.8*b*. Now we find a situation in which all the molecules of the gas are at one end of a larger container. There are many more possible ways that the total kinetic energy can be distributed among the molecules in the larger volume. That makes the configuration in Figure 19.8*b* extremely unlikely. The gas expands spontaneously to achieve a more probable (higher entropy) particle distribution.

TOOLS

Factors affecting entropy: volume changes

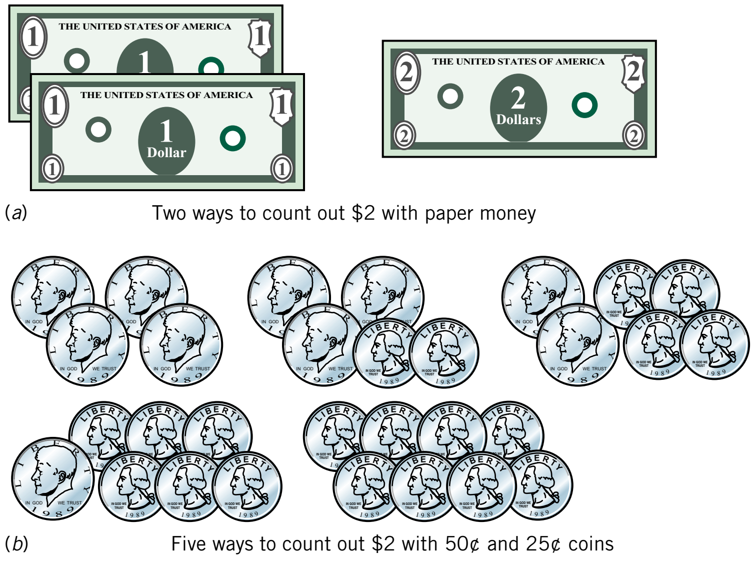
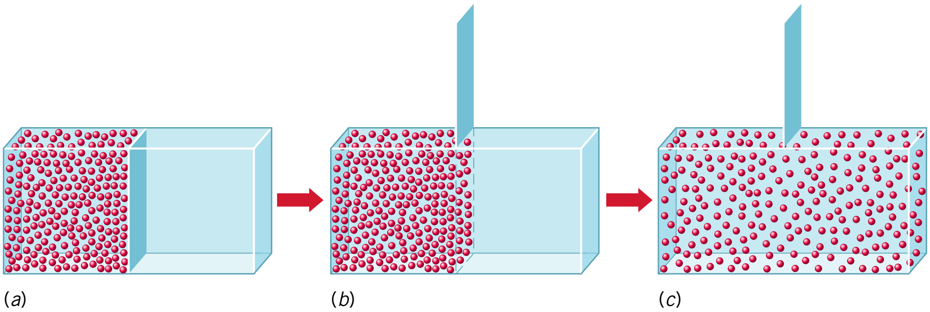

THE UNITED STATES OF AMERICA
1
Dollar
2
Dollars
(*a*) Two ways to count out $2 with paper money
(*b*) Five ways to count out $2 with 50¢ and 25¢ coins

Figure 19.7 | **Entropy.** If energy were money, entropy would describe the number of different ways of counting it out. For example, (*a*) there are only two ways of counting out $2 using American paper money, but (*b*) there are five ways of counting out $2 using 50 cent and 25 cent coins. One could consider a system using coins as having more entropy than a system using just paper money.

Figure 19.8 | **The expansion of a gas into a vacuum.** (*a*) A gas in a container separated from a vacuum by a partition. (*b*) The gas at the moment the partition is removed. (*c*) The gas expands to achieve a more probable (higher entropy) particle distribution.


(*a*) (*b*) (*c*)

Factors affecting entropy: temperature changes

Temperature

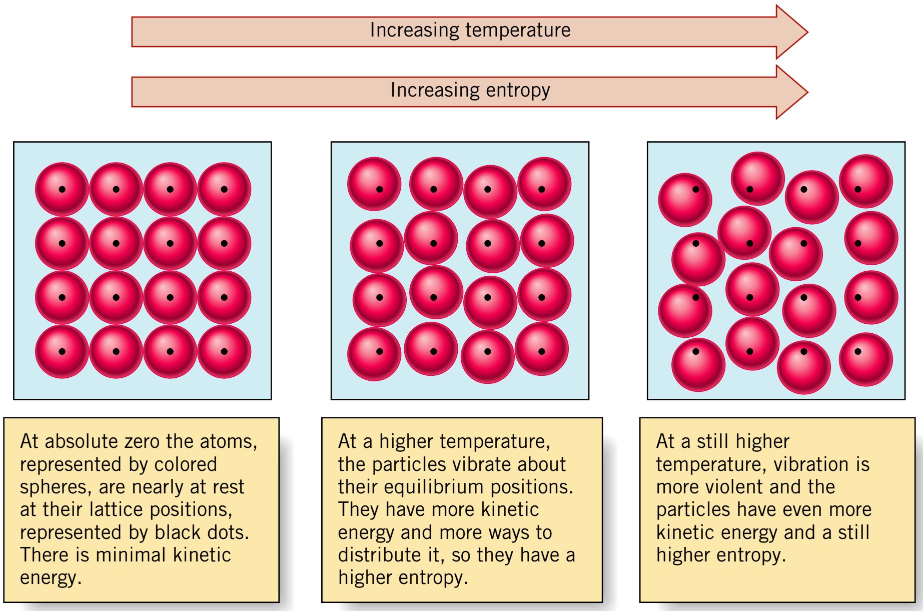
The entropy is also affected by the temperature; the higher the temperature the larger is the entropy. For example, when a substance is a solid at absolute zero, its particles are essentially motionless. There is relatively little kinetic energy, and so there are few ways to distribute kinetic energy among the particles, so the entropy of the solid is relatively low (Figure 19.9*a*). If some heat is added to the solid, the kinetic energy of the particles increases along with the temperature. This causes the particles to move and vibrate within the crystal, so at a particular moment (pictured in Figure 19.9*b*) the particles are not found exactly at their lattice sites. There is more kinetic energy than at the lower temperature, and there are more ways to distribute it among the molecules, so the entropy is larger. If the temperature is raised further, the particles are given even more kinetic energy with an even larger number of possible ways to distribute it, causing the solid to have a still higher entropy (Figure 19.9*c*).

Factors affecting entropy: physical state

Physical State

One of the major factors that affects the entropy of a system is its physical state, which is demonstrated in Figure 19.10. Suppose that the diagrams represent ice, water, and water vapor all at the same temperature. There is greater freedom of molecular movement in water than in ice at the same temperature, and so there are more ways to distribute kinetic energy among the molecules of liquid water than there are in ice. The water molecules in the vapor are free to move through the entire container. They are able to distribute their kinetic energies in a very large number of ways. In general, therefore, there are many more

Figure 19.9 | **Variation of entropy with temperature.** (*a*) At absolute zero the atoms, represented by colored circles, rest at their equilibrium lattice positions, represented by black dots. Entropy is relatively low. (*b*) At a higher temperature, the particles vibrate about their equilibrium positions and there are more different ways to distribute kinetic energy among the molecules. Entropy is higher than in (*a*). (*c*) At a still higher temperature, vibration is more violent and at any instant the particles are found in even more arrangements. Entropy is higher than in (*b*).



At absolute zero the atoms, represented by colored spheres, are nearly at rest at their lattice positions, represented by black dots. There is minimal kinetic energy.

At a higher temperature, the particles vibrate about their equilibrium positions. They have more kinetic energy and more ways to distribute it, so they have a higher entropy.

At a still higher temperature, vibration is more violent and the particles have even more kinetic energy and a still higher entropy.

(*a*) (*b*) (*c*)

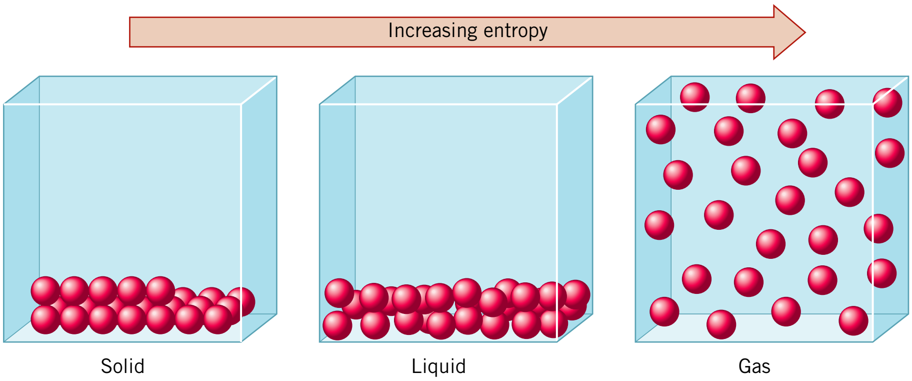


Figure 19.10 | **Comparison of the entropies of the solid, liquid, and gaseous states of a substance.** The crystalline solid has a very low entropy. The liquid has a higher entropy because its molecules can move more freely and there are more ways to distribute kinetic energy among them. All the particles are still found at one end of the container. The gas has the highest entropy because the particles are randomly distributed throughout the entire container, so there are many, many ways to distribute kinetic energy among the molecules.

possible ways to distribute kinetic energy among gas molecules than there are in liquids and solids. In fact, a gas has such a large entropy compared with a liquid or solid that changes which produce gases from liquids or solids are almost always accompanied by increases in entropy.

Number of Particles

Entropy, S, is an extensive property of a system just as H, the enthalpy, is an extensive property that depends on the amount of substance in the system. If we add more molecules to a system, there will be more ways to distribute the total energy of the system, and therefore the entropy is larger.

TOOLS

Factors affecting entropy: number of particles

Predicting the Sign of ΔS for a Chemical Reaction

When a chemical reaction produces or consumes gases, the sign of its entropy change is usually easy to predict. This is because the entropy of a gas is so much larger than that of either a liquid or solid. For example, the thermal decomposition of sodium bicarbonate produces two gases, CO_2 and H_2O.

$$2NaHCO_3(s) \xrightarrow{\text{heat}} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Because the amount of gaseous products is larger than the amount of gaseous reactants, we can predict that the entropy change for the reaction is positive. On the other hand, the reaction

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

(which can be used to remove sulfur dioxide from a gas mixture) has a negative entropy change because the number of gas molecules decreases as the reaction progresses.

For chemical reactions, another major factor that affects the sign of ΔS is a change in the total number of molecules as the reaction proceeds. When more molecules are produced during a reaction, more ways of distributing the energy among the molecules are possible. *When all other things are equal, reactions that increase the number of particles in the system tend to have a positive entropy change*, as shown in Figure 19.11.

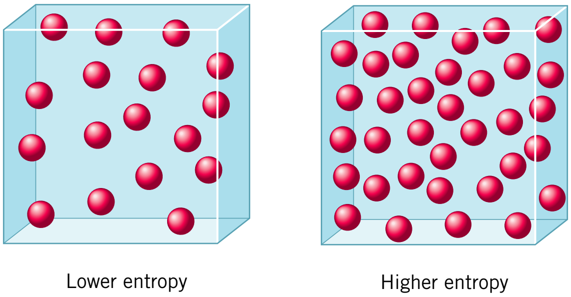


Figure 19.11 | **Entropy is affected by number of particles.** Adding additional particles to a system increases the number of ways that energy can be distributed in the system, so with all other things being equal, a reaction that produces more particles will have a positive value of ΔS.

Example 19.2
Predicting the Sign of ΔS

Predict the algebraic sign of ΔS for the reactions:

(a) $2NO_2(g) \longrightarrow N_2O_4(g)$

(b) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

■ **Analysis:** We will need to consider all of the factors that have an effect on the entropy change of the particular systems given to us. We note that all substances are in the gas phase, and no temperature change is specified. Therefore, phase change and temperature changes do not need to be considered.

■ **Assembling the Tools:** The tools we need are the factors that affect the entropy of a system when there are (1) changes in the number of gas molecules and (2) changes in the number of particles on going from reactants to products.

■ **Solution:** In reaction (a) we are forming fewer, more complex molecules (N_2O_4) from simpler ones (NO_2). Since we are forming fewer molecules, there are fewer ways to distribute energy among them, which means that the entropy must be decreasing. Therefore, ΔS must be negative. We reach the same conclusion by noting that one mole of gaseous product is formed from two moles of the gaseous reactant. When there is a decrease in the number of moles of gas, the reaction tends to have a negative ΔS.

For reaction (b), we can count the number of molecules on both sides. On the left of the equation we have six molecules; on the right there are seven. There are more ways to distribute kinetic energy among seven molecules than among six, so for reaction (b), we expect ΔS to be positive. We reach the same conclusion by counting the number of moles of gas on both sides of the equation. On the left there are 6 moles of gas; on the right there are 7 moles of gas. Because the number of moles of gas is increasing, we expect ΔS to be positive.

■ **Is the Answer Reasonable?** The only check we can perform here is to carefully review our reasoning. It appears sound, so the answers appear to be correct.

Practice Exercises

19.5 | Would you expect the ΔS to be positive or negative for the following:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

(*Hint*: How is the freedom of movement of the ions affected?)

19.6 | Predict the sign of the entropy change for (a) the condensation of steam to liquid water and (b) the sublimation of solid iodine.

19.7 | Predict the sign of ΔS for the following reactions:

(a) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(b) $CO(g) + 2H_2(g) \longrightarrow CH_3OH(g)$

19.8 | What is the expected sign of ΔS for the following reactions? Justify your answers.

(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(b) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(c) $Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$

19.4 | Second Law of Thermodynamics

You have learned that enthalpy and entropy are two factors that affect the spontaneity of a physical or chemical event. Sometimes they work together to favor a change, as in the combustion of gasoline where heat is given off (an exothermic change) and large volumes of gases are formed (an entropy increase).

In many situations, the enthalpy and entropy changes oppose each other, as in the melting of ice. Melting absorbs heat and is endothermic, which tends to make the process nonspontaneous. However, the greater freedom of motion of the molecules that accompanies melting has the opposite effect and tends to make the change spontaneous.

When the enthalpy and entropy changes conflict, temperature becomes a critical factor that can influence the direction in which the change is spontaneous. For example, consider a mixture of solid ice and liquid water. If we attempt to raise the temperature of the mixture to 25 °C, all the solid will melt. At 25 °C the change *solid* ⟶ *liquid* is spontaneous. On the other hand, if we attempt to cool the mixture to −25 °C, freezing occurs, so at −25 °C the opposite change, *liquid* ⟶ *solid*, is spontaneous. *Thus, there are actually three factors that can influence spontaneity: the enthalpy change, the entropy change, and the temperature.* The balance between these factors comes into focus through the second law of thermodynamics.

■ Knowledge of ΔS, ΔH, and T will allow us to determine if a system will undergo a spontaneous change.

Second Law of Thermodynamics

One of the most far-reaching observations in science is incorporated into the **second law of thermodynamics**, which states, in effect, that *whenever a spontaneous event takes place in our universe, the total entropy of the universe increases* ($\Delta S_{\text{total}} > 0$). Notice that the increase in entropy that's referred to here is for the *total* entropy of the *universe* (system *plus* surroundings), not just the system alone. This means that a system's entropy can decrease, just as long as there is a larger increase in the entropy of the surroundings so that the *overall* entropy change is positive. Because everything that happens relies on spontaneous changes of some sort, the entropy of the universe is constantly rising.

Now let's examine more closely the entropy change for the universe. As we've suggested, this quantity equals the sum of the entropy change for the system plus the entropy change for the surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

It can be shown that the entropy change for the surroundings is equal to the heat transferred *to* the surroundings *from* the system, $q_{\text{surroundings}}$, divided by the Kelvin temperature, T, at which it is transferred.

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

The law of conservation of energy requires that the heat transferred to the surroundings equals the negative of the heat added to the system, so we can write

$$q_{\text{surroundings}} = -\,q_{\text{system}}$$

In our study of the first law of thermodynamics we saw that for changes at constant temperature and pressure, $q_{\text{system}} = \Delta H$ for the system. By substitutions, therefore, we arrive at the relationship

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

and the entropy change for the entire universe becomes

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

By rearranging the right side of this equation, we obtain

$$\Delta S_{\text{total}} = \frac{T\,\Delta S_{\text{system}} - \Delta H_{\text{system}}}{T}$$

Now let's multiply both sides of the equation by T to give

$$T\,\Delta S_{\text{total}} = T\,\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

or

$$T\,\Delta S_{\text{total}} = -(\Delta H_{\text{system}} - T\,\Delta S_{\text{system}})$$

Because ΔS_{total} must be positive for a spontaneous change, the quantity in parentheses, $(\Delta H_{\text{system}} - T\,\Delta S_{\text{system}})$, must be negative. Therefore, we can state that for a change to be spontaneous,

$$\Delta H_{\text{system}} - T\,\Delta S_{\text{system}} < 0 \tag{19.2}$$

The Gibbs Free Energy

■ The origin of *free* in *free energy* is discussed in Section 19.7.

Equation 19.2 gives us a way of examining the balance between ΔH, ΔS, and temperature in determining the spontaneity of an event, and it becomes convenient at this point to introduce another thermodynamic state function. It is called the **Gibbs free energy, *G*,** named to honor one of America's greatest scientists, Josiah Willard Gibbs (1839–1903). (It's called *free energy* because it is related, as we will see later, to the maximum energy in a change that is "free" or "available" to do useful work.) The Gibbs free energy is defined as

$$G = H - TS \tag{19.3}$$

so for changes at constant T and P, this equation becomes

TOOLS

Gibbs free energy

$$\Delta G = \Delta H - T\,\Delta S \tag{19.4}$$

Because G is defined entirely in terms of state functions, it is also a state function. This means that

$$\Delta G = G_{\text{final}} - G_{\text{initial}} \tag{19.5}$$

By comparing Equations 19.2 and 19.4, we arrive at the special importance of the free energy change:

TOOLS

ΔG as a predictor of spontaneity

> At constant temperature and pressure, a change can only be spontaneous if it is accompanied by a decrease in the free energy of the system.

In other words, for a change to be spontaneous, G_{final} must be less than G_{initial} and ΔG must be negative. With this in mind, we can now examine how ΔH, ΔS, and T are related in determining spontaneity.

■ Reactions that occur with a free energy decrease are sometimes said to be **exergonic**. Those that occur with a free energy increase are sometimes said to be **endergonic**.

When ΔH Is Negative and ΔS Is Positive

The combustion of octane (a component of gasoline),

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

is a very exothermic reaction. There is also a large increase in entropy because the number of particles in the system increases and large volumes of gases are formed. For this change, ΔH is negative and ΔS is positive, both of which favor spontaneity. Let's analyze how this affects the sign of ΔG.

$$\begin{aligned} &\Delta H \text{ is negative } (-) \\ &\Delta S \text{ is positive } (+) \\ &\Delta G = \Delta H - T\,\Delta S \\ &\quad\;\; = (-) - [T(+)] \end{aligned}$$

Notice that regardless of the absolute temperature, which must be a positive number, ΔG will be negative. This means that regardless of the temperature, such a change must be spontaneous. In fact, once started, fires will continue to consume all available fuel or oxygen at nearly any temperature because combustion reactions are always spontaneous (see Figure 19.12*a*).

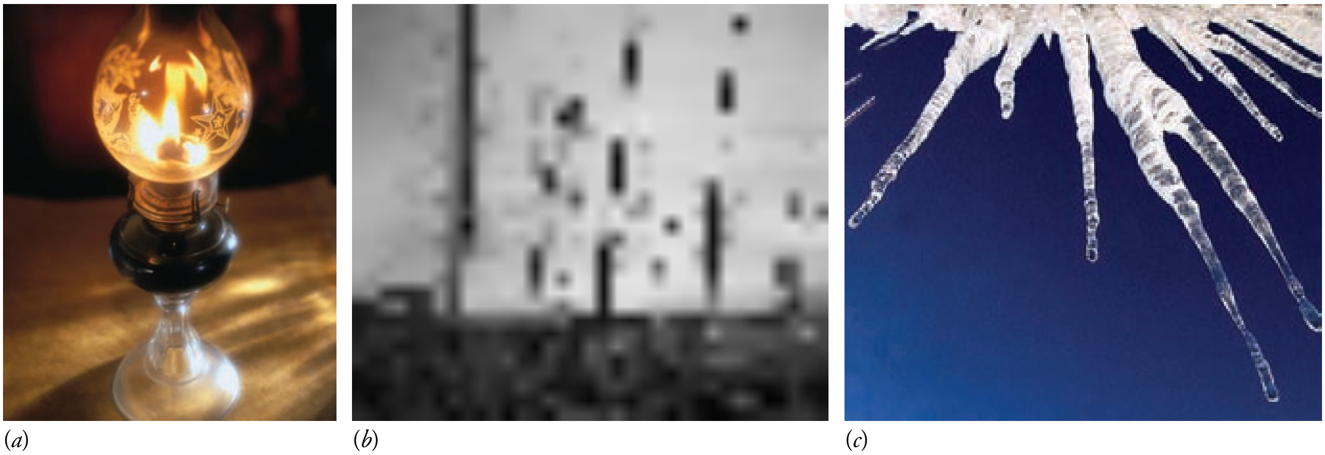

(*a*) (*b*) (*c*)

Figure 19.12 | **Process spontaneity can be predicted if ΔH, ΔS, and T are known.** (*a*) When ΔH is negative and ΔS is positive, as in any combustion reaction, the reaction is spontaneous at any temperature. (*b*) When ΔH is positive and ΔS is negative, the process is not spontaneous. Left to themselves, ash, carbon dioxide, and water will not spontaneously combine to form wood. (*c*) When ΔH and ΔS have the same sign, temperature determines whether the process is spontaneous or not. Water spontaneously becomes ice below 0 °C, and ice spontaneously melts into liquid water above 0 °C. *(a: Corbis Images; b: iStockphoto; c: John Berry/The Image Works)*

When ΔH Is Positive and ΔS Is Negative

When a change is endothermic and is accompanied by a lowering of the entropy, both factors work against spontaneity.

$$\begin{aligned}&\Delta H \text{ is positive } (+)\\&\Delta S \text{ is negative } (-)\\&\Delta G = \Delta H - T\Delta S\\&\quad\;\, = (+) - [T(-)]\end{aligned}$$

Now, no matter what the temperature is, ΔG will be positive and the change must be nonspontaneous. An example would be carbon dioxide and water coming back together to form wood and oxygen again in a fire (Figure 19.12*b*).[1] If you saw such a thing happen in a video, such as on YouTube, experience would tell you that the video was being played backwards.

When ΔH and ΔS Have the Same Sign

When ΔH and ΔS have the same algebraic sign, the temperature becomes the determining factor in controlling spontaneity. If ΔH and ΔS are both positive, then

$$\Delta G = (+) - [T(+)]$$

Thus, ΔG is the difference between two positive quantities, ΔH and $T\Delta S$. This difference will only be negative if the term $T\Delta S$ is larger in magnitude than ΔH, and this will only be true when the temperature is high. In other words, *when ΔH and ΔS are both positive, the change will be spontaneous at high temperature but not at low temperature.* A change noted above is the melting of ice.

$$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$$

---

[1] Plants can manufacture wood from carbon dioxide and water that they take in, but the reaction by itself is *not* spontaneous. Plant cells manufacture wood by coupling this nonspontaneous reaction to a complex series of reactions with negative values of ΔG, so that the entire chain of reactions *taken together* is spontaneous overall. This same trick is used to drive nonspontaneous processes forward in human cells. The high negative free energy change from the breakdown of sugar and other nutrients is coupled with the nonspontaneous synthesis of complex proteins from simple starting materials, driving cell growth and making life possible.

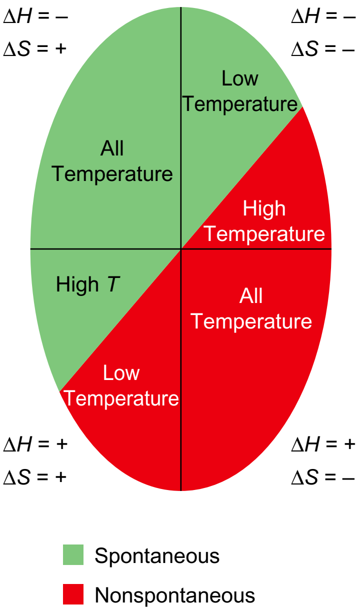


Figure 19.13 | **Summary of the effects of the signs of ΔH and ΔS on spontaneity as a function of temperature.** When ΔH and ΔS have the same sign, spontaneity is determined by the temperature.

This is a change that is endothermic and also accompanied by an increase in entropy. We know that at high temperature (above 0 °C) melting is spontaneous, but at low temperature (below 0 °C) it is not.

For similar reasons, when ΔH and ΔS are both negative, ΔG will be negative (and the change spontaneous) only when the temperature is low.

$$\Delta G = (-) - [T(-)]$$

Only when the negative value of ΔH is larger in magnitude than the negative value of $T\,\Delta S$ will ΔG be negative. Such a change is only spontaneous at low temperature. An example is the freezing of water (see Figure 19.12*c*).

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(s)$$

This is an exothermic change that is accompanied by an decrease in entropy; it is only spontaneous at low temperatures (i.e., below 0 °C).

Figure 19.13 summarizes the effects of the signs of ΔH and ΔS on ΔG, and hence on the spontaneity of physical and chemical events.

19.5 | Third Law of Thermodynamics

Earlier we described how the entropy of a substance depends on temperature, and we noted that at absolute zero the order within a crystal is a maximum and the entropy is a minimum. The **third law of thermodynamics** goes one step farther by stating: *At absolute zero the entropy of a perfectly ordered pure crystalline substance is zero.*

$$S = 0 \quad \text{at} \quad T = 0\ \mathrm{K}$$

Because we know the point at which entropy has a value of zero, it is possible by *experimental measurement* and calculation to determine the total amount of entropy that a substance has at temperatures above 0 K.

■ 25 °C and 1 atm are the same standard conditions we used in our discussion of $\Delta H°$ in Chapter 7.

If the entropy of one mole of a substance is determined at a temperature of 298 K (25 °C) and a pressure of 1 atm, we call it the **standard entropy, $S°$**. Table 19.1 lists the standard entropies for a number of substances.[2] Notice that entropy has the dimensions of energy/temperature (i.e., joules per kelvin); this is explained in *Chemistry Outside the Classroom 19.1.*

Calculating $\Delta S°$ for a Reaction

Once we have the standard entropies of a variety of substances, we can calculate the **standard entropy change, $\Delta S°$**, for chemical reactions in much the same way as we calculated $\Delta H°$ in Chapter 7.

TOOLS

Standard entropy changes

$$\Delta S° = (\text{sum of } S° \text{ of the products}) - (\text{sum of } S° \text{ of the reactants}) \qquad \textbf{(19.6)}$$

■ This is simply a Hess's law type of calculation. Note, however, that elements have nonzero $S°$ values, which must be included in the bookkeeping.

If the reaction we are working with happens to correspond to the formation of 1 mol of a compound from its elements, then the $\Delta S°$ that we calculate can be referred to as the **standard entropy of formation, $\Delta S_f°$**. Values of $\Delta S_f°$ are not tabulated, however; if we need them for some purpose, we must calculate them from tabulated values of $S°$.

---

[2] In our earlier discussions of standard states (Chapter 7) we defined the *standard pressure* as 1 atm. This was the original pressure unit used by thermodynamicists. However, in the SI, the recognized unit of pressure is the pascal (Pa), not the atmosphere. After considerable discussion, the SI adopted the **bar** as the standard pressure for thermodynamic quantities: 1 bar = 10^5 Pa. One bar differs from one atmosphere by only 1.3%, and for thermodynamic quantities that we deal with in this text, their values at 1 atm and at 1 bar differ by an insignificant amount. Since most available thermodynamic data is still specified at 1 atm rather than 1 bar, we shall continue to use 1 atm for the standard pressure.

Table 19.1 Standard Entropies of Some Typical Substances at 298.15 K

Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})
$Ag(s)$	42.55	$CaO(s)$	40	$N_2(g)$	191.5
$AgCl(s)$	96.2	$Ca(OH)_2(s)$	76.1	$NH_3(g)$	192.5
$Al(s)$	28.3	$CaSO_4(s)$	107	$NH_4Cl(s)$	94.6
$Al_2O_3(s)$	51.0	$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	131	$NO(g)$	210.6
$C(s)$ (graphite)	5.69	$CaSO_4 \cdot 2H_2O(s)$	194.0	$NO_2(g)$	240.5
$CO(g)$	197.9	$Cl_2(g)$	223.0	$N_2O(g)$	220.0
$CO_2(g)$	213.6	$Fe(s)$	27	$N_2O_4(g)$	304
$CH_4(g)$	186.2	$Fe_2O_3(s)$	90.0	$Na(s)$	51.0
$CH_3Cl(g)$	234.2	$H_2(g)$	130.6	$Na_2CO_3(s)$	136
$CH_3OH(l)$	126.8	$H_2O(g)$	188.7	$NaHCO_3(s)$	102
$CO(NH_2)_2(s)$	104.6	$H_2O(l)$	69.96	$NaCl(s)$	72.38
$CO(NH_2)_2(aq)$	173.8	$HCl(g)$	186.7	$NaOH(s)$	64.18
$C_2H_2(g)$	200.8	$HNO_3(l)$	155.6	$Na_2SO_4(s)$	149.4
$C_2H_4(g)$	219.8	$H_2SO_4(l)$	157	$O_2(g)$	205.0
$C_2H_6(g)$	229.5	$HC_2H_3O_2(l)$	160	$PbO(s)$	67.8
$C_8H_{18}(l)$	466.9	$Hg(l)$	76.1	$S(s)$	31.9
$C_2H_5OH(l)$	161	$Hg(g)$	175	$SO_2(g)$	248.5
$Ca(s)$	41.4	$K(s)$	64.18	$SO_3(g)$	256.2
$CaCO_3(s)$	92.9	$KCl(s)$	82.59		
$CaCl_2(s)$	114	$K_2SO_4(s)$	176		

Example 19.3
Calculating $\Delta S°$ from Standard Entropies

Urea (a compound found in urine) is manufactured commercially from CO_2 and NH_3. One of its uses is as a fertilizer, where it reacts slowly with water in the soil to produce ammonia and carbon dioxide. The ammonia provides a source of nitrogen for growing plants.

$$\underset{\text{urea}}{CO(NH_2)_2(aq)} + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

What is the standard entropy change when one mole of urea reacts with water?

■ **Analysis:** We need to combine standard entropies in the correct way to represent what occurs in the chemical reaction. We will use the principles just presented in this section. We can notice the similarity to the methods we learned for the determination of standard heats of reaction in Chapter 7.

■ **Assembling the Tools:** We need to use Equation 19.6 to compute the standard entropy change for the reaction. To do this we need the balanced chemical equation, above, and the data found in Table 19.1 that is listed in the table below.

Substance	$S°$ (J mol^{-1} K^{-1})
$CO(NH_2)_2(aq)$	173.8
$H_2O(l)$	69.96
$CO_2(g)$	213.6
$NH_3(g)$	192.5

CHEMISTRY OUTSIDE THE CLASSROOM 19.1

Carved in Stone

In 1870 Ludwig von Boltzmann (Figure 1) started developing the ideas and concepts that led to the modern field of science called statistical mechanics. Statistical mechanics describes the properties of large groups of particles based on the laws of probability and how the particles interact.

Figure 1 Ludwig von Boltzmann (February 20, 1844 to September 5, 1906) *(Hulton Archive /Getty Images, Inc.)*

In developing this field, Boltzmann developed his famous equation for entropy,

$$S = k \ln W$$

which is indeed carved in stone at his gravesite in Vienna, Austria (Figure 2). The equation states that the entropy of a particle is equal to the Boltzmann constant, $k = 1.38 \times 10^{-23}$ J mol^{-1} K^{-1}, times the natural logarithm of W, the number of different microstates that the particle can visit. The combination of the properties of all the microstates defines the macrostate, or state, of the system, which we observe on the basis of pressure, volume, temperature, and number of particles. Describing and counting microstates is beyond the scope of our discussion. However, two interesting results of Boltzmann's equation can be described easily.

First, let's consider a simple system, a perfect crystal of one of the elements. In such a crystal, there is only one arrangement of the atoms, often face-centered or body-centered cubic as shown in Chapter 12. Now let's lower the temperature to absolute zero. Since the temperature is directly proportional to the kinetic energy, this suggests that the kinetic energy, or movement, of the atoms is zero. (Quantum mechanics tells us this is not quite true.) However, the result is that a perfect crystal at 0 K has only one possible microstate, a totally ordered arrangement of all the atoms. Solving the Boltzmann equation when $W = 1$ tells us the entropy must be zero for a perfect crystal at absolute zero. This is the third law of thermodynamics.

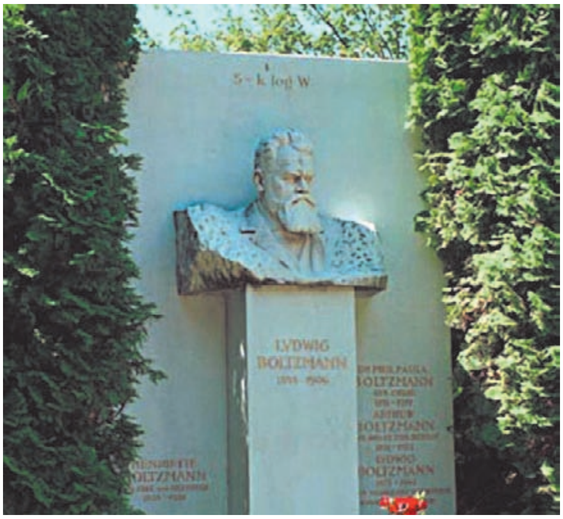


Figure 2 A photo of the gravesite of Boltzmann with his equation engraved above his bust. *(Frantisek Zboray)*

A second case of interest involves entropy change. If we consider an ideal gas in a container, it will have some number of microstates, W_{initial}, that define its pressure, volume, temperature, and number of gas molecules. After the change we will have a new number of microstates, W_{final}. We can now write an equation for entropy change as

$$\begin{aligned}\Delta S &= k \ln W_{\text{final}} - k \ln W_{\text{initial}} \\ &= k \ln (W_{\text{final}} / W_{\text{initial}})\end{aligned}$$

For an ideal gas, the microstates are defined on the basis of the position and momentum of the particles. If we expand the gas isothermally, the temperature, and therefore momentum, mv, of the particles does not change. However, the number of positions that a particle can visit will change in direct proportion to the volume change. For example, if we take one mole of an ideal gas and triple its volume the entropy change will be

$$\begin{aligned}\Delta S &= (1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}) \times \ln (3) \\ &= 1.52 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}\end{aligned}$$

For a mole of substance we multiply by Avogadro's number

$$\Delta S = \left(\frac{1.52 \times 10^{-23} \text{ J}}{\text{molecule K}}\right)\left(\frac{6.02 \times 10^{-23} \text{ molecules}}{\text{mole}}\right)$$

$$\Delta S = 9.13 \text{ J mol}^{-1} \text{ K}^{-1}$$

Since we expanded one mole of gas, the entropy change is 9.13 J K^{-1}.

Solution: Applying Equation 19.6, we have

$$\begin{aligned}\Delta S^\circ &= \left[S^\circ_{CO_2(g)} + 2S^\circ_{NH_3(g)}\right] - \left[S^\circ_{CO(NH_2)_2(aq)} + S^\circ_{H_2O(l)}\right]\\ &= \left[1\ \cancel{\text{mol}} \times \left(\frac{213.6\ \text{J}}{\cancel{\text{mol}}\ \text{K}}\right) + 2\ \cancel{\text{mol}} \times \left(\frac{192.5\ \text{J}}{\cancel{\text{mol}}\ \text{K}}\right)\right]\\ &\quad - \left[1\ \cancel{\text{mol}} \times \left(\frac{173.8\ \text{J}}{\cancel{\text{mol}}\ \text{K}}\right) + 1\ \cancel{\text{mol}} \times \left(\frac{69.96\ \text{J}}{\cancel{\text{mol}}\ \text{K}}\right)\right]\\ &= (598.6\ \text{J/K}) - (243.8\ \text{J/K})\\ &= 354.8\ \text{J/K}\end{aligned}$$

■ Notice that the unit *mol* cancels in each term, so the units of ΔS° are joules per kelvin.

Thus, the standard entropy change for this reaction is +354.8 J/K (which we can also write as +354.8 J K^{-1}).

Is the Answer Reasonable? In the reaction, gases are formed from liquid reactants. Since gases have much larger entropies than liquids, we expect ΔS° to be positive, which agrees with our answer.

Practice Exercises

19.9 | Calculate ΔS°_f for $NH_3(g)$. (*Hint*: Write the equation for the reaction; see Section 7.8.)

19.10 | Calculate the standard entropy change, ΔS°, in J K^{-1} for the following reactions:

(a) $CaO(s) + 2HCl(g) \longrightarrow CaCl_2(s) + H_2O(l)$

(b) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

19.6 | Standard Free Energy Change, ΔG°

When ΔG is determined at 25 °C (298 K) and 1 atm, we call it the **standard free energy change,**[3] **ΔG°.** There are several ways of obtaining ΔG° for a reaction. One of them is to compute ΔG° from ΔH° and ΔS° using an expression analogous to Equation 19.4.

$$\Delta G^\circ = \Delta H^\circ - (298.15\ \text{K})\,\Delta S^\circ$$

TOOLS

Calculating ΔG° from ΔH° and ΔS°

Experimental measurement of ΔG° is also possible, but we will discuss how this is done later.

Example 19.4
Calculating ΔG° from ΔH° and ΔS°

Calculate ΔG° for the reaction of urea with water from values of ΔH° and ΔS°.

$$CO(NH_2)_2(aq) + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

Analysis: This problem has two parts. From Chapter 7 we found out how to calculate the standard heat of reaction, ΔH°, and in this chapter we found out how to determine ΔS°. Once we have ΔH° and ΔS°, we need to combine them in the correct way to obtain ΔG°.

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[3] Sometimes, the temperature is specified as a subscript in writing the symbol for the standard free energy change. For example, ΔG° can also be written ΔG°_{298}. As you will see later, there are times when it is desirable to indicate the temperature explicitly.

Assembling the Tools: We can calculate $\Delta G°$ with the equation

$$\Delta G° = \Delta H° - 298.15 \text{ K } \Delta S°$$

Before calculating any values we need the balanced chemical equation, which is given in the statement of the problem. To calculate $\Delta H°$, we can use Hess's law as a tool with the data in Table 7.2. To obtain $\Delta S°$, we normally would need to do a similar calculation using Equation 19.6 as a tool with data from Table 19.1. However, we already performed this calculation in Example 19.3.

Solution: First we calculate $\Delta H°$ from data in Table 7.2.

$$\begin{aligned}\Delta H° &= \left[\Delta H°_{\text{f } CO_2(g)} + 2\Delta H°_{\text{f } NH_3(g)}\right] - \left[\Delta H°_{\text{f } CO(NH_2)_2(aq)} + \Delta H°_{\text{f } H_2O(l)}\right] \\ &= \left[1 \cancel{\text{mol}} \times \left(\frac{-393.5 \text{ kJ}}{\cancel{\text{mol}}}\right) + 2 \cancel{\text{mol}} \times \left(\frac{-46.19 \text{ kJ}}{\cancel{\text{mol}}}\right)\right] \\ &\quad - \left[1 \cancel{\text{mol}} \times \left(\frac{-319.2 \text{ kJ}}{\cancel{\text{mol}}}\right) + 1 \cancel{\text{mol}} \times \left(\frac{-285.9 \text{ kJ}}{\cancel{\text{mol}}}\right)\right] \\ &= (-485.9 \text{ kJ}) - (-605.1 \text{ kJ}) \\ &= +119.2 \text{ kJ}\end{aligned}$$

In Example 19.3 we found $\Delta S°$ to be $+354.8 \text{ J K}^{-1}$. To calculate $\Delta G°$ we also need the Kelvin temperature, which we must express to at least four significant figures to match the number of significant figures in $\Delta S°$. Since standard temperature is *exactly* 25 °C, $T_K = (25.00 + 273.15) \text{ K} = 298.15 \text{ K}$. Also, we must be careful to express the energy units of $\Delta H°$ and $T\Delta S°$ with the same SI prefix so they combine correctly. We'll change $\Delta S°$ from $+354.8 \text{ J K}^{-1}$ to $+0.3548 \text{ kJ K}^{-1}$. Substituting into the equation for $\Delta G°$,

$354.8 \text{ J K}^{-1} = 0.3548 \text{ kJ K}^{-1}$

$$\begin{aligned}\Delta G° &= +119.2 \text{ kJ} - (298.15 \cancel{\text{K}})(0.3548 \text{ kJ } \cancel{\text{K}^{-1}}) \\ &= +119.2 \text{ kJ} - 105.8 \text{ kJ} \\ &= +13.4 \text{ kJ}\end{aligned}$$

Therefore, for this reaction, $\Delta G° = +13.4$ kJ.

Is the Answer Reasonable? There's not much we can do to check the reasonableness of the answer. We just need to check to be sure we've done the calculations correctly.

Practice Exercises

19.11 | Calculate $\Delta G°$ for the formation of one mole of N_2O_4 from its elements using $\Delta H_f°$ and $\Delta S_f°$ for N_2O_4. (*Hint*: Write the chemical equation.)

19.12 | Use the data in Table 7.2 and Table 19.1 to calculate $\Delta G°$ for the formation of iron(III) oxide (the iron oxide in rust). The equation for the reaction is

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

In Section 7.8 you learned that it is useful to have tabulated standard heats of formation, $\Delta H_f°$, because they can be used with Hess's law to calculate $\Delta H°$ for many different reactions. **Standard free energies of formation, $\Delta G_f°$,** can be used in similar calculations to obtain $\Delta G°$ for a reaction or physical change.

TOOLS

Calculating $\Delta G°$ using $\Delta G_f°$ values

$$\Delta G° = (\text{sum of } \Delta G_f° \text{ of products}) - (\text{sum of } \Delta G_f° \text{ of reactants}) \qquad (19.7)$$

The $\Delta G_f°$ values for some typical substances are listed in Table 19.2. Example 19.5 shows how we can use them to calculate $\Delta G°$ for a reaction.

Table 19.2 Standard Free Energies of Formation of Typical Substances at 298.15 K

Substance	$\Delta G_f°$ (kJ mol^{-1})	Substance	$\Delta G_f°$ (kJ mol^{-1})	Substance	$\Delta G_f°$ (kJ mol^{-1})
$Ag(s)$	0	$CaO(s)$	−604.2	$K_2SO_4(s)$	−1316.4
$AgCl(s)$	−109.7	$Ca(OH)_2(s)$	−896.76	$N_2(g)$	0
$Al(s)$	0.00	$CaSO_4(s)$	−1320.3	$NH_3(g)$	−16.7
$Al_2O_3(s)$	−1576.4	$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	−1435.2	$NH_4Cl(s)$	−203.9
$C(s)$ (graphite)	0	$CaSO_4 \cdot 2H_2O(s)$	−1795.7	$NO(g)$	+ 86.69
$CO(g)$	−137.3	$Cl_2(g)$	0	$NO_2(g)$	+51.84
$CO_2(g)$	−394.4	$Fe(s)$	0	$N_2O(g)$	+103.6
$CH_4(g)$	−50.79	$Fe_2O_3(s)$	−741.0	$N_2O_4(g)$	+98.28
$CH_3Cl(g)$	−58.6	$H_2(g)$	0	$Na(s)$	0
$CH_3OH(l)$	−166.2	$H_2O(g)$	−228.6	$Na_2CO_3(s)$	−1048
$CO(NH_2)_2(s)$	−197.2	$H_2O(l)$	−237.2	$NaHCO_3(s)$	−851.9
$CO(NH_2)_2(aq)$	−203.8	$HCl(g)$	−95.27	$NaCl(s)$	−384.0
$C_2H_2(g)$	+209	$HNO_3(l)$	−79.91	$NaOH(s)$	−382
$C_2H_4(g)$	+68.12	$H_2SO_4(l)$	−689.9	$Na_2SO_4(s)$	−1266.8
$C_2H_6(g)$	−32.9	$HC_2H_3O_2(l)$	−392.5	$O_2(g)$	0
$C_2H_5OH(l)$	−174.8	$Hg(l)$	0	$PbO(s)$	−189.3
$C_8H_{18}(l)$	+17.3	$Hg(g)$	+31.8	$S(s)$	0
$Ca(s)$	0	$K(s)$	0	$SO_2(g)$	−300.4
$CaCO_3(s)$	−1128.8	$KCl(s)$	−408.3	$SO_3(g)$	−370.4
$CaCl_2(s)$	−750.2				

Example 19.5
Calculating $\Delta G°$ from $\Delta G_f°$

Ethanol, C_2H_5OH, is made from grain by fermentation and is used as an additive to gasoline to produce a fuel mix called E85 (85% ethanol, 15% gasoline). What is $\Delta G°$ for the combustion of liquid ethanol to give $CO_2(g)$ and $H_2O(g)$?

E85
85% Ethanol

(© AP/Wide World Photos)

■ **Analysis:** The process for determining $\Delta G°$ is the same as we used for determining $\Delta H°$ and $\Delta S°$. Before we do anything, the balanced chemical equation will be needed.

■ **Assembling the Tools:** Our tool is Equation 19.7.

$$\Delta G° = (\text{sum of } \Delta G_f° \text{ of products}) - (\text{sum of } \Delta G_f° \text{ of reactants})$$

To use it we will need the balanced chemical equation for the reaction and $\Delta G_f°$ for each reactant and product. The free energy data are available in Table 19.2.

■ **Solution:** First, we write the balanced equation for the reaction.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

Applying Equation 19.7, we have

$$\Delta G^\circ = [2\Delta G^\circ_{\text{f }CO_2(g)} + 3\Delta G^\circ_{\text{f }H_2O(g)}] - [\Delta G^\circ_{\text{f }C_2H_5OH(l)} + 3\Delta G^\circ_{\text{f }O_2(g)}]$$

As with ΔH°_f, the ΔG°_f for any element in its standard state is zero. Therefore, using the data from Table 19.2,

$$\begin{aligned}\Delta G^\circ &= \left[2\ \cancel{\text{mol}} \times \left(\frac{-394.4\text{ kJ}}{\cancel{\text{mol}}}\right) + 3\ \cancel{\text{mol}} \times \left(\frac{-228.6\text{ kJ}}{\cancel{\text{mol}}}\right)\right] - \left[1\ \cancel{\text{mol}} \times \left(\frac{-174.8\text{ kJ}}{\cancel{\text{mol}}}\right) + 3\ \cancel{\text{mol}} \times \left(\frac{0\text{ kJ}}{\cancel{\text{mol}}}\right)\right] \\ &= (-1474.6\text{ kJ}) - (-174.8\text{ kJ}) \\ &= -1299.8\text{ kJ}\end{aligned}$$

The standard free energy change for the reaction equals −1299.8 kJ.

■ **Is the Answer Reasonable?** This is a combustion reaction for a compound containing only C, H and O. Very often, such combustion reactions are spontaneous with negative values for ΔG°. Our answer is obviously in the right ballpark.

Practice Exercises

19.13 | Calculate ΔG° for the reaction of iron(III) oxide with carbon monoxide to give elemental iron and carbon dioxide. (*Hint*: Be careful writing the balanced chemical equation.)

19.14 | Calculate $\Delta G^\circ_\text{reaction}$ in kilojoules for the following reactions using the data in Table 19.2.

(a) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(b) $Ca(OH)_2(s) + 2HCl(g) \longrightarrow CaCl_2(s) + 2H_2O(g)$

19.7 | Maximum Work and ΔG

One of the chief uses of spontaneous chemical reactions is the production of useful work. For example, fuels are burned in gasoline or diesel engines to power automobiles and heavy machinery, and chemical reactions in batteries start our autos and run all sorts of modern electronic gadgets, including cell phones, iPods, and laptop computers.

When chemical reactions occur, however, their energy is not always harnessed to do work. For instance, if gasoline is burned in an open dish, the energy evolved is lost entirely as heat and no useful work is accomplished. Engineers, therefore, seek ways to capture as much energy as possible in the form of work. One of their primary goals is to maximize the efficiency with which chemical energy is converted to work and to minimize the amount of energy transferred unproductively to the environment as heat.

■ Gas and diesel engines are not very efficient, so most of the energy produced in the combustion of fuel appears as heat, not work. That's why these engines require cooling systems.

Scientists have discovered that the maximum conversion of chemical energy to work occurs if a reaction is carried out under conditions that are said to be thermodynamically reversible. A process is defined as **thermodynamically reversible** if its driving force is opposed by another force that is just the slightest bit weaker, so that the slightest increase in the opposing force will cause the direction of the change to be reversed. An example of a nearly reversible process is illustrated in Figure 19.14, where we have a compressed gas in a cylinder pushing against a piston that's held in place by liquid water above it. If a water molecule evaporates, the external pressure drops slightly and the gas can expand just a bit, performing a small amount of work. Gradually, as one water molecule after another evaporates, the gas inside the cylinder slowly expands and performs work on the

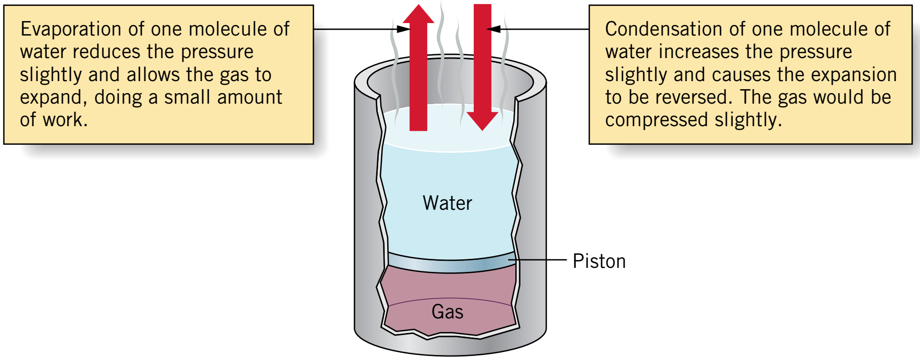
Evaporation of one molecule of water reduces the pressure slightly and allows the gas to expand, doing a small amount of work.
Condensation of one molecule of water increases the pressure slightly and causes the expansion to be reversed. The gas would be compressed slightly.
Water
Piston
Gas

Figure 19.14 | **A reversible expansion of a gas.** As water molecules evaporate one at a time, the external pressure gradually decreases and the gas slowly expands, performing a small amount of work in each step. The process would be reversed if a molecule of water were to condense into the liquid. The ability of the expansion to be reversed by the slightest increase in the opposing pressure is what makes this a reversible process.

surroundings. At any time, however, the process can be reversed by the condensation of a water molecule.[4]

Although we could obtain the maximum work by carrying out a change reversibly, a thermodynamically reversible process requires so many steps that it proceeds at an extremely slow speed. If the work cannot be done at a reasonable rate, it is of little value to us. Our goal, then, is to approach thermodynamic reversibility for maximum efficiency, but to carry out the change at a pace that will deliver work at acceptable rates.

The relationship of useful work to thermodynamic reversibility was illustrated earlier (Section 7.5) in our discussion of the discharge of an automobile battery. Recall that when the battery is shorted with a heavy wrench, no work is done and all the energy appears as heat. In this case there is nothing opposing the discharge, and it occurs in the most thermodynamically irreversible manner possible. However, when the current is passed through a small electric motor, the motor itself offers resistance to the passage of the electricity and the discharge takes place slowly. In this instance, the discharge occurs in a more nearly thermodynamically reversible manner because of the opposition provided by the motor, and a relatively large amount of the available energy appears in the form of the work accomplished by the motor.

The preceding discussion leads naturally to the question: Is there a limit to the amount of the available energy in a reaction that can be harnessed as useful work? The answer to this question is to be found in the Gibbs free energy.

> The maximum amount of energy produced by a reaction that can be *theoretically* harnessed as work is equal to ΔG.

This is the energy that need not be lost to the surroundings as heat and is therefore *free* to be used for work. Thus, by determining the value of ΔG, we can find out whether or not a given reaction will be an effective source of useful energy. Also, by comparing the actual amount of work derived from a given system with the ΔG values for the reactions involved, we can measure the efficiency of the system.

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[4] Although we sometimes say that a chemical reaction is "reversible" because it can run in both the forward and reverse directions, we cannot say the reaction is *thermodynamically reversible* unless the concentrations are only infinitesimally different from their equilibrium values as the reaction occurs.

ON THE CUTTING EDGE 19.2

Thermodynamic Efficiency and Sustainability

The concept of sustainability incorporates the idea that the human race must consider the cumulative effects of our everyday activities and reinvent these activities so that we will not drive ourselves into extinction. It has been stated that 99.9% of all species that ever lived are now extinct. Humans have the possibility, because of our ability to think and plan, to avoid this fate. Chemists, physicists, and biologists will be very important in developing the tools that will make this effort successful.

Table 1 Efficiencies of Various Devices

Tungsten lightbulb	2–3%
Candle	0.04%
Gas mantle	0.2%
Light-emitting diode	Up to 22%
Fluorescent tube	Up to 15%
Compact fluorescent	Up to 12%
Electric motors	75 to 90%

Thermodynamics enters this discussion because it sets limits on our ability to use resources. For instance, the first law of thermodynamics suggests that a change in internal energy is the sum of the work and heat changes in the system. If work is the useful part of an energy change and heat is wasted energy, we can say that $w/(q + w)$ is the efficiency of the system. There are other measures of efficiency. For example Nicolas Léonard Sadi Carnot suggested that the efficiency of a heat engine is $(T_{\text{high}} - T_{\text{low}})/T_{\text{high}}$, where the high temperature exists inside the engine and the low temperature is the temperature of the exhaust. The best Carnot efficiency is realized in engines that have the greatest possible difference between the operating temperature and the waste heat temperature. Table 2 lists the efficiencies of some heat engines.

Engineers and research scientists realize that one part of realizing a sustainable energy economy is to maximize efficiency.

Figure 1 Combustion produces energy with a low efficiency and increased amounts of pollutants. *(© AP/Wide World Photos)*

Figure 2 Wind turbines convert wind energy to electricity with little on-site pollution. *(Henry Georgi/Aurora Photos Inc.)*

Table 2 Approximate Heat Engine Efficiencies

Gasoline engines	25–30%
Steam engines	8%
Diesel engines	40%
Steam turbines	60%

Modern sustainability calculations of efficiency include, along with the thermodynamic efficiency, the costs of all components of the process. For an electric generating facility, it includes the cost of the land that the facility uses, the cost of constructing the facility, the cost of waste disposal, and the cost of environmental impacts such as CO_2, NO_x, SO_2, and heat emissions to the environment. Employee, management, and regulatory costs are also included. The difficulty in sustainability calculations is finding an appropriate method for adding all these factors into a final, meaningful value.

With the modern realization of the many factors that comprise a simple activity such as the generation of electricity, there are many opportunities for chemists and other scientists to make significant contributions. Advanced lubricants can help increase the efficiency of many mechanical devices. Chemists and materials scientists design and fabricate materials that can withstand extremely high temperatures for long periods of time. Durable materials increase efficiency by reducing the "down-time" for frequent repairs. Although tungsten has a melting point of 3683 K it is not used in electric turbines because it is too brittle. However, tungsten nitride and silicon nitride are used successfully as very durable coatings in high-temperature generators. These same materials are used in the turbines of modern jet engines in commercial aircraft. (Figure 3.)

Figure 3 Cutaway of a jet engine showing high-speed, high-temperature turbine blades. *(Nick Lewis Photography/Alamy)*

Example 19.6

Calculating Maximum Work

Calculate the maximum work available, expressed in kilojoules, from the oxidation of 1 mol of octane, $C_8H_{18}(l)$, by oxygen to give $CO_2(g)$ and $H_2O(l)$ at 25 °C and 1 atm.

Analysis: The maximum work is equal to ΔG for the reaction. Standard thermodynamic conditions are specified, so we need to determine $\Delta G°$.

Assembling the Tools: The tool for this calculation is Equation 19.7.

$$\Delta G° = (\text{sum of } \Delta G_f° \text{ of products}) - (\text{sum of } \Delta G_f° \text{ of reactants})$$

Solution: First, we need a balanced equation for the reaction. For the complete oxidation (combustion) of one mole of C_8H_{18} we have

$$C_8H_{18}(l) + 12\tfrac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$$

Then we apply Equation 19.7:

$$\Delta G° = [8\Delta G°_{f\,CO_2(g)} + 9\Delta G°_{f\,H_2O(l)}] - [\Delta G°_{f\,C_8H_{18}(l)} + 12.5\Delta G°_{f\,O_2(g)}]$$

Referring to Table 19.2 and dropping the canceled mol units,

$$\begin{aligned}\Delta G° &= [8 \times (-394.4)\text{ kJ} + 9 \times (-237.2)\text{ kJ}] - [1 \times (+17.3)\text{ kJ} + 12.5 \times (0)\text{ kJ}]\\ &= (-5290\text{ kJ}) - (+17.3\text{ kJ})\\ &= -5307\text{ kJ}\end{aligned}$$

Thus, at 25 °C and 1 atm, we can expect no more than 5307 kJ of work from the oxidation of 1 mol of C_8H_{18}.

Is the Answer Reasonable? Be sure to check the algebraic signs of each of the terms in the calculation. Also check that the stoichiometric coefficients multiply the correct $\Delta G°$ values. Finally, be sure that the correct $\Delta G°$ value for the liquid state of water is used. Since the table lists $\Delta G°$ values for two states of water, liquid and gas, this is a common source of error.

Figure 19.15 | **Blastoff of the space shuttle.** The large negative heat of formation of Al_2O_3 provides power to the solid-state booster rockets that lift the space shuttle from its launch pad. *(NASA)*

Practice Exercises

19.15 | Calculate the maximum work that could be obtained from the combustion of 125 g of ethanol, $C_2H_5OH(l)$. How does it compare with the maximum work from the combustion of 125 g of $C_8H_{18}(l)$? Which is the better fuel? (*Hint*: The work available *per mole* has already been calculated in the worked examples.)

19.16 | Calculate the maximum work that could be obtained at 25 °C and 1 atm from the oxidation of 1.00 mol of aluminum by $O_2(g)$ to give $Al_2O_3(s)$. (The combustion of aluminum in booster rockets provides part of the energy that lifts the space shuttle off its launching pad, Figure 19.15.)

19.8 | Free Energy and Equilibrium

We have seen that when the value of ΔG for a given change is negative, the change occurs spontaneously. We have also seen that a change is nonspontaneous when ΔG is positive. However, when ΔG is neither positive nor negative, the change is neither spontaneous nor nonspontaneous—the system is in a state of equilibrium. This occurs when ΔG is equal to zero.

> When a system is in a state of dynamic equilibrium,
>
> $$G_{\text{products}} = G_{\text{reactants}} \quad \text{and} \quad \Delta G = 0$$

Let's again consider the freezing of water:

$$H_2O(l) \rightleftharpoons H_2O(s)$$

Below 0 °C, ΔG for this change is negative and the freezing is spontaneous. On the other hand, above 0 °C we find that ΔG is positive and freezing is nonspontaneous. When the temperature is exactly 0 °C, $\Delta G = 0$ and an ice–water mixture exists in a condition of equilibrium. As long as heat isn't added or removed from the system, neither freezing nor melting is spontaneous and the ice and liquid water can exist together indefinitely.

Equilibrium and Work

We have identified ΔG as a quantity that specifies the amount of work that is available from a system. Since ΔG is zero at equilibrium, the amount of work available is zero also. Therefore, when a system is at equilibrium, no work can be extracted from it. As an example, consider again the common lead storage battery that we use to start our cars.

When the battery is fully charged, there are virtually no products of the discharge reaction present. The chemical reactants, however, are present in large amounts. Therefore, the total free energy of the reactants far exceeds the total free energy of products and, since $\Delta G = G_{\text{products}} - G_{\text{reactants}}$, the ΔG of the system has a large negative value. This means that a lot of energy is available to do work. As the battery discharges, the reactants are converted to products and G_{products} gets larger while $G_{\text{reactants}}$ gets smaller; thus ΔG becomes less negative, and less energy is available to do work. Finally, the battery reaches equilibrium. The total free energies of the reactants and the products have become equal, so $G_{\text{products}} - G_{\text{reactants}} = 0$ and $\Delta G = 0$. No further work can be extracted and we say the battery is "dead."

Estimating Melting and Boiling Points

For a phase change such as $H_2O(l) \longrightarrow H_2O(s)$, equilibrium can only exist at one particular temperature at atmospheric pressure. For water, that temperature is 0 °C. Above 0 °C, only liquid water can exist, and below 0 °C all the liquid will freeze to give ice. This yields an interesting relationship between ΔH and ΔS for a phase change. Since $\Delta G = 0$,

$$\Delta G = 0 = \Delta H - T\Delta S$$

Therefore,

$$\Delta H = T\Delta S$$

and

$$\Delta S = \frac{\Delta H}{T} \tag{19.8}$$

Thus, if we know ΔH for the phase change and the temperature at which the two phases coexist, we can calculate ΔS for the phase change. Another interesting relationship that we can obtain is

$$T = \frac{\Delta H}{\Delta S} \tag{19.9}$$

Thus, if we know ΔH and ΔS, we can calculate the temperature at which equilibrium will occur.

Example 19.7
Calculating the Equilibrium Temperature for a Phase Change

For the phase change $Br_2(l) \longrightarrow Br_2(g)$, $\Delta H° = +31.0 \text{ kJ mol}^{-1}$ and $\Delta S° = 92.9 \text{ J mol}^{-1} \text{ K}^{-1}$. Assuming that ΔH and ΔS are nearly temperature independent, calculate the approximate Celsius temperature at which $Br_2(l)$ will be in equilibrium with $Br_2(g)$ at 1 atm (i.e., the normal boiling point of liquid Br_2).

■ **Analysis:** The normal boiling point of a substance is the temperature at which the liquid and gas phases are in equilibrium at one atmosphere of pressure; see Section 12.6. The wording of the problem strongly suggests that we can substitute $\Delta H°$ and $\Delta S°$ for ΔH and ΔS, respectively. If we do that we can use the equations we just discussed.

■ **Assembling the Tools:** The temperature at which equilibrium exists is given by Equation 19.9. When we assume that ΔH and ΔS do not depend much on temperature, then we can use $\Delta H°$ and $\Delta S°$ in this equation to approximate the boiling point. That is,

$$T \approx \frac{\Delta H°}{\Delta S°}$$

■ ΔH and ΔS do not change much with changes in temperature. This is because temperature changes affect the enthalpies and entropies of both the reactants and products by about the same amount, so the differences between reactants and products stays fairly constant.

■ **Solution:** Substituting the data given in the problem,

$$\begin{aligned} T &\approx \frac{3.10 \times 10^4 \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}{92.9 \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}\ \text{K}^{-1}} \\ &= 334 \text{ K} \end{aligned}$$

The Celsius temperature is 334 − 273 = 61 °C. Notice that we were careful to express $\Delta H°$ in joules, not kilojoules, so the units would cancel correctly. It is also interesting that the boiling point we calculated is quite close to the measured normal boiling point of 58.8 °C.

■ **Is the Answer Reasonable?** The $\Delta H°$ value equals 31,000 and the $\Delta S°$ value equals approximately 100, which means the temperature should be about 310 K. Our value, 334 K, is not far from that, so the answer is reasonable.

Practice Exercises

19.17 | The heat of vaporization of ammonia is 21.7 kJ mol^{-1} and the boiling point of ammonia is −33.3 °C. Estimate the entropy change for the vaporization of liquid ammonia. (*Hint*: What algebraic sign do we expect for this entropy change?)

19.18 | The heat of vaporization of mercury is 60.7 kJ/mol. For $Hg(l)$, $S° = 76.1 \text{ J mol}^{-1} \text{ K}^{-1}$, and for $Hg(g)$, $S° = 175 \text{ J mol}^{-1} \text{ K}^{-1}$. Estimate the normal boiling point of liquid mercury.

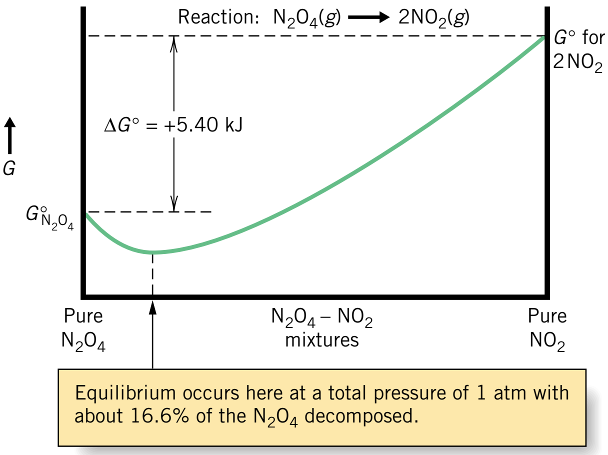
Free Energy Diagrams

One way to gain a better understanding of how the free energy changes during a reaction is by studying **free energy diagrams**. As an example, let's study a reaction you've seen before—the decomposition of N_2O_4 into NO_2.

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

In our discussion of chemical equilibrium in Chapter 15 (page 698), we noted that equilibrium in this system can be approached from *either* direction, with the same equilibrium concentrations being achieved provided we begin with the same overall system composition.

Figure 19.16 | **Free energy diagram for the decomposition of $N_2O_4(g)$.** The minimum on the curve indicates the composition of the reaction mixture at equilibrium. Because $\Delta G°$ is positive, the position of equilibrium lies close to the reactants. Not much product will form by the time the system reaches equilibrium.



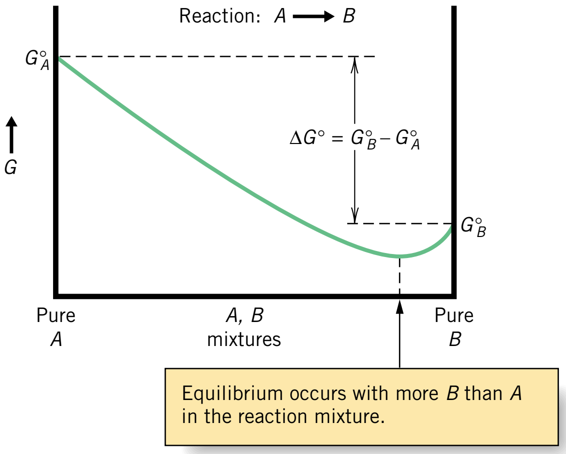
Equilibrium occurs here at a total pressure of 1 atm with about 16.6% of the N_2O_4 decomposed.

Figure 19.16 shows the free energy diagram for the reaction, which depicts how the free energy changes as we proceed from the reactant to the product. On the left of the diagram we have the free energy of one mole of pure $N_2O_4(g)$, and on the right the free energy of two moles of pure $NO_2(g)$. Points along the horizontal axis represent mixtures of both substances. Notice that in going from reactant (N_2O_4) to product ($2NO_2$), the free energy has a minimum. It drops below that of either pure N_2O_4 or pure NO_2.

Any system will spontaneously seek the lowest point on its free energy curve. If we begin with pure $N_2O_4(g)$, the reaction will proceed from left to right and some $NO_2(g)$ will be formed, because proceeding in the direction of NO_2 leads to a lowering of the free energy. If we begin with pure $NO_2(g)$, a change also will occur. Going downhill on the free energy curve now takes place as the reverse reaction occurs [i.e., $2NO_2(g) \longrightarrow N_2O_4(g)$]. Once the bottom of the "valley" is reached, the system has come to equilibrium. As you learned in Sections 12.9 and 15.6, if the system isn't disturbed, the composition of the equilibrium mixture will remain constant. Now we see that the reason is because any change (moving either to the left or right) would require an uphill climb. Free energy increases are not spontaneous, so this doesn't happen.

■ When a system moves "downhill" on its free energy curve, $G_{\text{final}} < G_{\text{initial}}$ and ΔG is negative. Changes with negative ΔG are spontaneous.

An important thing to notice in Figure 19.16 is that some reaction takes place spontaneously in the forward direction even though $\Delta G°$ is positive. However, the reaction doesn't proceed far before equilibrium is reached. For comparison, Figure 19.17 shows the shape of the free energy curve for a reaction with a negative $\Delta G°$. We see here that at equilibrium there has been a much greater conversion of reactants to products. Thus, *$\Delta G°$ tells us where the position of equilibrium lies between pure reactants and pure products.*



Equilibrium occurs with more *B* than *A* in the reaction mixture.

Figure 19.17 | **Free energy curve for a reaction having a negative $\Delta G°$.** Because $G°_B$ is lower than $G°_A$, $\Delta G°$ is negative. This causes the position of equilibrium to lie far to the right, near the products. When the system reaches equilibrium, there will be a large amount of products present and few reactants.

Δ*G*° and the Position of Equilibrium

- When Δ*G*° is positive, the position of equilibrium lies close to the reactants and little reaction occurs by the time equilibrium is reached. The reaction will appear to be nonspontaneous.
- When Δ*G*° is negative, the position of equilibrium lies close to the products and a large amount of products will have formed by the time equilibrium is reached. The reaction will appear to be spontaneous.
- When $\Delta G° = 0$, the position of equilibrium will lie about midway between reactants and products. Substantial amounts of both reactants and products will be present when equilibrium is reached. The reaction will appear to be spontaneous whether we begin with pure reactants or pure products.

TOOLS

Using Δ*G*° to assess the position of equilibrium

Δ*G*° and the Position of Equilibrium

In general, the value of Δ*G*° for most reactions is much larger numerically than the Δ*G*° for the $N_2O_4 \longrightarrow NO_2$ reaction. In addition, the extent to which a reaction proceeds is very sensitive to the size of Δ*G*°. If the Δ*G*° value for a reaction is reasonably large—about 20 kJ or more—almost no observable reaction will occur when Δ*G*° is positive. On the other hand, the reaction will go almost to completion if Δ*G*° is both large and negative.[5] From a practical standpoint, then, *the size and sign of* Δ*G*° *serve as indicators of whether an observable spontaneous reaction will occur.*

Example 19.8

Using Δ*G*° as a Predictor of the Outcome of a Reaction

Would we expect to be able to observe the following reaction at 25 °C?

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

Analysis: To answer this question we need to know the magnitude and algebraic sign of Δ*G*°; that will allow us to estimate the position of equilibrium.

Assembling the Tools: The relationship between Δ*G*° and the position of equilibrium is one tool needed to answer this question. The other tool is Equation 19.7, which is needed to obtain the standard free energy change, Δ*G*°.

Solution: First, let's calculate Δ*G*° for the reaction using the data in Table 19.2. The procedure is the same as that discussed earlier.

$$\begin{aligned}\Delta G° &= [G°_{\mathrm{f\,NH_3}(g)} + \Delta G°_{\mathrm{f\,HCl}(g)}] - [G°_{\mathrm{f\,NH_4Cl}(s)}] \\ &= [(-16.7\text{ kJ}) + (-95.27\text{ kJ})] - [-203.9\text{ kJ}] \\ &= +91.9\text{ kJ}\end{aligned}$$

Because Δ*G*° is large and positive, only extremely small amounts of products can form at this temperature. Therefore, we would not expect to observe any decomposition of the NH_4Cl.

Is the Answer Reasonable? Be sure to check the algebraic signs of each term in the calculation. Also check that the free energies of the reactants are subtracted from those of the products. This problem involves adding (and subtracting) numbers. If we add all the raw numbers, without regard to sign, that should be our maximum possible positive answer. Similarly, the negative of this sum will be the largest possible negative value we could have. Our answer easily passes that test.

---

[5] As we discussed earlier, to actually see a change take place, the speed of a spontaneous reaction must be reasonably fast. For example, the decomposition of the nitrogen oxides into N_2 and O_2 is thermodynamically spontaneous (Δ*G*° is negative), but their rates of decomposition are so slow that these substances appear to be stable, and some are obnoxious air pollutants.

Practice Exercises

19.19 | Use the data in Table 19.2 to determine whether the reaction

$$SO_2(g) + O_2(g) \longrightarrow SO_3(g)$$

should "occur spontaneously" at 25 °C. (*Hint*: Be careful with algebraic signs.)

19.20 | Use the data in Table 19.2 to determine whether we should expect to see the formation of $CaCO_3(s)$ in the following reaction at 25 °C.

$$CaCl_2(s) + H_2O(g) + CO_2(g) \longrightarrow CaCO_3(s) + 2HCl(g)$$

$\Delta G°$ Varies with Temperature

So far, we have confined our discussion of the relationship of free energy and equilibrium to a special case, 25 °C. But what about other temperatures? Equilibria certainly can exist at temperatures other than 25 °C, and in Chapter 15 you learned how to apply Le Châtelier's principle to predict the way temperature affects the position of equilibrium. Now let's see how thermodynamics deals with this.

You've learned that at 25 °C the position of equilibrium is determined by the difference between the free energy of pure products and the free energy of pure reactants. This difference is given by $\Delta G°_{298}$, where we have now used the subscript "298" to indicate the temperature, 298 K. We define $\Delta G°_{298}$ as

$$\Delta G°_{298} = (G°_{\text{products}})_{298} - (G°_{\text{reactants}})_{298}$$

At temperatures other than 25 °C, it is still the difference between the free energies of the products and reactants that determines the position of equilibrium. We write this as $\Delta G°_T$. Thus, at a temperature other than 25 °C (298 K), we have

$$\Delta G°_T = (G°_{\text{products}})_T - (G°_{\text{reactants}})_T$$

where $(G°_{\text{products}})_T$ and $(G°_{\text{reactants}})_T$ are the total free energies of the pure products and reactants, respectively, at this other temperature.

Next, we must find a way to compute $\Delta G°_T$. Earlier we saw that $\Delta G°$ can be obtained from the equation

$$\Delta G° = \Delta H° - (298 \text{ K})\, \Delta S°$$

At a different temperature, T, the equation becomes

$$\Delta G°_T = \Delta H°_T - T\,\Delta S°_T$$

Now we seem to be getting closer to our goal. If we can compute or estimate the values of $\Delta H°_T$ and $\Delta S°_T$ for a reaction, we have solved our problem.

The size of $\Delta G°_T$ obviously depends very strongly on the temperature—the equation above has temperature as one of its variables. However, as noted in the margin comment on page 895, the magnitudes of the ΔH and ΔS for a reaction are relatively insensitive to changes in temperature. Therefore, we can use $\Delta H°_{298}$ and $\Delta S°_{298}$ as reasonable approximations of $\Delta H°_T$ and $\Delta S°_T$. This allows us to rewrite the equation for $\Delta G°_T$ as

Calculating $\Delta G°$ at temperatures other than 25 °C

$$\Delta G°_T \approx \Delta H°_{298} - T\,\Delta S°_{298} \tag{19.10}$$

The following example illustrates how this equation is useful.

Example 19.9

$\Delta G°$ at Temperatures Other than 25 °C

Earlier we saw that at 25 °C the value of $\Delta G°$ for the reaction

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

has a value of +5.40 kJ. What is the approximate value of $\Delta G_T°$ for this reaction at 105 °C?

Analysis: In this problem we can't calculate $\Delta G°$ from standard free energies of formation because we only have such values for 25 °C. Therefore, we're going to have to use the alternative approach described above, which requires Equation 19.10 and values of $\Delta H°$ and $\Delta S°$.

Assembling the Tools: Equation 19.10 is the tool needed to solve the problem. To use it, we need values of $\Delta H°$ and $\Delta S°$. The $\Delta H°$ is calculated using Equation 7.13, Hess's law. The $\Delta S°$ is determined using Equation 19.6.

Using the data in Table 7.2 on page 285 we find the following standard heats of formation for use in Equation 7.13.

$$\begin{array}{ll} N_2O_4(g) & \Delta H_f° = +9.67 \text{ kJ/mol} \\ NO_2(g) & \Delta H_f° = +33.8 \text{ kJ/mol} \end{array}$$

Next, we compute $\Delta S°$ for the reaction using absolute entropy data from Table 19.1.

$$\begin{array}{ll} N_2O_4(g) & S° = 304 \text{ J/mol K} \\ NO_2(g) & S° = 240.5 \text{ J/mol K} \end{array}$$

Solution: First, we compute $\Delta H°$ using Hess's law and the data we just gathered:

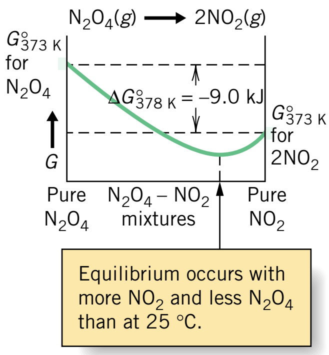
$$\begin{aligned} \Delta H° &= [2\Delta H°_{f\,NO_2(g)}] - [\Delta H°_{f\,N_2O_4(g)}] \\ &= \left[2\ \cancel{\text{mol}} \times \left(\frac{33.8 \text{ kJ}}{\cancel{\text{mol}}}\right)\right] - \left[1\ \cancel{\text{mol}} \times \left(\frac{9.67 \text{ kJ}}{\cancel{\text{mol}}}\right)\right] \\ &= +57.9 \text{ kJ} \end{aligned}$$

Next, we use Equation 19.6 to calculate $\Delta S°$

$$\begin{aligned} \Delta S° &= \left[2\ \cancel{\text{mol}} \times \left(\frac{240.5 \text{ J}}{\cancel{\text{mol}} \text{ K}}\right)\right] - \left[1\ \cancel{\text{mol}} \times \left(\frac{304 \text{ J}}{\cancel{\text{mol}} \text{ K}}\right)\right] \\ &= +177 \text{ J K}^{-1} \text{ or } 0.177 \text{ kJ K}^{-1} \end{aligned}$$

The temperature is 105 °C, which is 378 K, so we can write the free energy change as $\Delta G_{378}°$. Substituting into Equation 19.10 using $T = 378$ K, we have

$$\begin{aligned} \Delta G_{378}° &\approx (+57.9 \text{ kJ}) - (378\ \cancel{\text{K}})(0.177 \text{ kJ } \cancel{\text{K}^{-1}}) \\ &\approx -9.0 \text{ kJ} \end{aligned}$$


$N_2O_4(g) \longrightarrow 2NO_2(g)$
$G_{373\text{ K}}°$ for N_2O_4
$\Delta G_{378\text{ K}}° = -9.0$ kJ
$G_{373\text{ K}}°$ for $2NO_2$
G
Pure N_2O_4
$N_2O_4 - NO_2$ mixtures
Pure NO_2

Equilibrium occurs with more NO_2 and less N_2O_4 than at 25 °C.

Notice that the $\Delta G_T°$ has changed from +5.40 kJ at 25 °C to −9.0 at 105 °C.

Is the Answer Reasonable? As usual, we can double-check the algebraic signs to be sure we've performed the calculations correctly. For this problem, however, we can check that our answer makes sense based on Le Châtelier's principle.

Since the reaction is endothermic, heat may be written as a reactant:

$$\text{Heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

When heat is added, we expect the position of equilibrium to shift toward the products. The positive value of ΔG_T° at 25 °C means that the position of equilibrium lies nearest the reactants. When ΔG_T° has a negative value at 105 °C, it means that the position of equilibrium now lies closer to the products. The result is a shift in the position of equilibrium toward the products, in agreement with our expectations.

Practice Exercises

19.21 | In Example 19.4 we computed ΔH° and ΔS° for the reaction

$$CO(NH_2)_2(aq) + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

What is ΔG_T° for this reaction at 75 °C? (*Hint*: Be careful with the units.)

19.22 | Use the data in Table 19.2 to determine ΔG_{298}° for the reaction

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Then calculate the approximate value for ΔG_{490}° for the reaction at 217 °C using the data in Tables 7.2 and 19.1. How does the position of equilibrium for this reaction change as the temperature is increased?

19.9 | Equilibrium Constants and ΔG°

In the preceding discussion, you learned in a qualitative way that the position of equilibrium in a reaction is determined by the sign and magnitude of ΔG°. You also learned that the direction in which a reaction proceeds depends on where the system composition stands relative to the minimum on the free energy curve. Thus, the reaction will proceed spontaneously in the forward direction only if it will lead to a lowering of the free energy (i.e., if ΔG is negative).

Quantitatively, the relationship between ΔG and ΔG° is expressed by the following equation, which we will not attempt to justify.

TOOLS

Relating the reaction quotient to ΔG

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{19.11}$$

Here R is the gas constant in appropriate energy units (i.e., 8.314 J mol^{-1} K^{-1}), T is the Kelvin temperature, and ln Q is the natural logarithm of the reaction quotient that was introduced in Section 15.2. For gaseous reactions, Q is calculated using partial pressures expressed in atm;[6] for reactions in solution, Q is calculated from molar concentrations. Equation 19.11 allows us to predict the direction of the spontaneous change in a reaction mixture if we know ΔG° and the composition of the mixture, as illustrated in Example 19.10.

■ In Chapter 15 we defined Q as the *reaction quotient*, the numerical value of the mass action expression.

Example 19.10
Determining the Direction of a Spontaneous Reaction

The reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $\Delta G_{298}^\circ = -5.40$ kJ per mole of N_2O_4. In a reaction mixture, the partial pressure of NO_2 is 0.25 atm and the partial pressure of N_2O_4 is 0.60 atm. In which direction must this reaction proceed, at 25 °C, to reach equilibrium?

■ In Chapter 15, you learned that you can also predict the direction of a reaction by comparing Q with K (page 723).

■ **Analysis:** Since we know that reactions proceed spontaneously *toward* equilibrium, we are really being asked to determine whether the reaction will proceed spontaneously in the forward or reverse direction. In Chapter 15 we learned that when we compare Q to K we can determine in which direction a reaction will proceed. Determining the sign of ΔG will also allow us to predict the direction of a chemical reaction.

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[6] Strictly speaking, we should express pressures in atm or bar depending on which was used to obtain the ΔG° data. For simplicity, we will use the more familiar pressure unit atm in all our calculations. Because the atm and bar differ by only about 1 percent, any errors that might be introduced will be very small.

■ **Assembling the Tools:** We can use Equation 19.11 to calculate ΔG for the forward reaction. If ΔG is negative, then the forward reaction is spontaneous. However, if the calculated ΔG is positive, the forward reaction is nonspontaneous and it is really the reverse reaction that is spontaneous. To solve Equation 19.11 we need the correct form for the mass action expression so we can calculate Q. Expressed in terms of partial pressures, the mass action expression defines Q for this reaction:

$$Q = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

■ **Solution:** Using the mass action expression for Q, the equation we will use is

$$\Delta G = \Delta G° + RT \ln\left(\frac{P_{N_2O_4}}{P_{NO_2}^2}\right)$$

Next, let's assemble the data:

$$\begin{aligned} \Delta G°_{298} &= -5.40 \text{ kJ mol}^{-1} & T &= 298 \text{ K} \\ &= -5.40 \times 10^3 \text{ J mol}^{-1} & P_{N_2O_4} &= 0.60 \text{ atm} \\ R &= 8.314 \text{ J mol}^{-1} \text{K}^{-1} & P_{NO_2} &= 0.25 \text{ atm} \end{aligned}$$

Notice that we have changed the energy units of $\Delta G°$ to joules so they will be the same as the energy units in the R we are using. The next step is to substitute the data into the equation for ΔG. In doing this, we leave off the units for the partial pressures because reaction quotients are always unitless quantities.[7] Here is the calculation.[8]

$$\begin{aligned} \Delta G &= -5.40 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1}\ \cancel{\text{K}^{-1}})\ (298\ \cancel{\text{K}})\ \ln\left[\frac{0.60}{(0.25)^2}\right] \\ &= -5.40 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1}\ \cancel{\text{K}^{-1}})(298\ \cancel{\text{K}})\ \ln(9.6) \\ &= -5.40 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1}\ \cancel{\text{K}^{-1}})(298\ \cancel{\text{K}})(2.26) \\ &= -5.40 \times 10^3 \text{ J mol}^{-1} + 5.60 \times 10^3 \text{ J mol}^{-1} \\ &= +2.0 \times 10^2 \text{ J mol}^{-1} \end{aligned}$$

Since ΔG is positive, the forward reaction is nonspontaneous. The reverse reaction is the one that will occur, and to reach equilibrium, some N_2O_4 will have to decompose.

■ **Is the Answer Reasonable?** There is no simple check. However, we can check to be sure the energy units in both terms on the right are the same. Notice that here we have changed the units for $\Delta G°$ to joules to match those of R. Also notice that the temperature is expressed in kelvins, to match the temperature units in R.

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[7] For reasons beyond the scope of this text, quantities in mass action expressions used to compute reaction quotients and equilibrium constants are actually ratios. For partial pressures, it's the pressure in atm divided by 1 atm; for concentrations, it's the molarity divided by 1 *M*. This causes the units to cancel to give a unitless value for Q or K.

[8] As we noted in the footnote on page 655, when taking the logarithm of a quantity, the number of digits *after the decimal point* should equal the number of significant figures in the quantity. Since 0.60 atm and 0.25 atm both have two significant figures, the logarithm of the quantity in square brackets (2.26) is rounded to give two digits after the decimal point.

Practice Exercises

19.23 | Calculate ΔG for the reaction described in the preceding example if the partial pressure of NO_2 is 0.260 atm and the partial pressure of N_2O_4 is 0.598 atm. Where does the system stand relative to equilibrium? (*Hint*: What is ΔG for a system at equilibrium?)

19.24 | In which direction will the reaction described in Example 19.10 proceed to reach equilibrium if the partial pressure of NO_2 is 0.60 atm and the partial pressure of N_2O_4 is 0.25 atm?

Computing Thermodynamic Equilibrium Constants

Earlier you learned that when a system reaches equilibrium the free energy of the products equals the free energy of the reactants and ΔG equals zero. We also know that at equilibrium the reaction quotient equals the equilibrium constant.

$$\text{At equilibrium} \quad \begin{cases} \Delta G = 0 \\ Q = K \end{cases}$$

If we substitute these into Equation 19.11, we obtain

$$0 = \Delta G^\circ + RT \ln K$$

Determining thermodynamic equilibrium constants

which can be rearranged to give

$$\Delta G^\circ = -RT \ln K \tag{19.12}$$

The equilibrium constant K calculated from this equation is called the **thermodynamic equilibrium constant** and corresponds to K_p for reactions involving gases (with partial pressures expressed in atm) and to K_c for reactions in solution (with concentrations expressed in mol L^{-1}).[9]

Equation 19.12 is useful because it permits us to determine equilibrium constants from either measured or calculated values of ΔG°. As you know, ΔG° can be determined by a Hess's law type of calculation from tabulated values of ΔG_f°. It also allows us to obtain values of ΔG° from measured equilibrium constants.

Example 19.11
Calculating the Gibbs Free Energy Change

The brownish haze often associated with air pollution is caused by nitrogen dioxide, NO_2, a red-brown gas. Nitric oxide, NO, is formed in automobile engines and some of it escapes into the air where it is oxidized to NO_2 by oxygen.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The value of K_p for this reaction is 1.7×10^{12} at 25.00 °C. What is ΔG° for the reaction, (a) expressed in joules per mole and (b) in kilojoules per mole?

■ **Analysis:** We have an equation that relates the equilibrium constant to the standard free energy. All we have to do is collect the appropriate information to perform the calculation.

---

[9] The thermodynamic equilibrium constant requires that gases *always* be included as partial pressures in mass action expressions. The pressure units must be standard pressure units (atmospheres or bars, depending on which convention was used for collecting the ΔG° data. For a heterogeneous equilibrium involving a gas and a substance in solution, the mass action expression will mix partial pressures (for the gas) with molarities (for the dissolved substance).

Assembling the Tools: The relationship between the standard free energy change, $\Delta G°$, and an equilibrium constant is expressed in Equation 19.12.

$$\Delta G° = -RT \ln K_p$$

We'll need the data below to calculate $\Delta G°$. Note that the temperature is given to the nearest hundredth of a degree, so we'll use $T_K = t_C + 273.15$ to compute the Kelvin temperature.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$T = 298.15 \text{ K}$$
$$K_p = 1.7 \times 10^{12}$$

Solution: (a) Substituting these values into the equation, we have

$$\begin{aligned}\Delta G° &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}) \ln (1.7 \times 10^{12}) \\ &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}) \times (28.16) \\ &= -6.980 \times 10^4 \text{ J mol}^{-1} \text{ (to four significant figures)}\end{aligned}$$

(b) Changing J to kJ,

$$\Delta G° = -69.80 \text{ kJ mol}^{-1}$$

Is the Answer Reasonable? The value of K_p tells us that the position of equilibrium lies far to the right, which means $\Delta G°$ must be large and negative. Therefore, the answer, -69.80 kJ mol^{-1}, seems reasonable.

The units in this calculation give $\Delta G°$ on a per mole (mol^{-1}) basis. This reminds us that we are viewing the coefficients of the reactants and products as representing moles, rather than some other sized quantity.

Example 19.12
Thermodynamic Equilibrium Constants

Sulfur dioxide, which is sometimes present in polluted air, reacts with oxygen when it passes over the catalyst in automobile catalytic converters. The product is the very acidic oxide, sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

For this reaction, $\Delta G° = -1.40 \times 10^2$ kJ mol^{-1} at 25 °C. What is the value of K_p?

Analysis: Once again we have an equation that we can solve once we collect all of the data for the equation's variables.

Assembling the Tools: We will use Equation 19.12.

$$\Delta G° = -RT \ln K_p$$

The chemical equation, in this case, is extra information. We see from the equation that we need to find T and $\Delta G°$ in the statement of the problem, and if necessary look up the value for R. We can list our data as

$$\begin{aligned}R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ T &= 298 \text{ K} \\ \Delta G° &= -1.40 \times 10^2 \text{ kJ mol}^{-1} \\ &= -1.40 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

To make the units cancel correctly, we have added the unit mol^{-1} to the value of $\Delta G°$. This just emphasizes that the amounts of reactants and products are specified in mole-sized quantities.

Solution: To calculate K_p, let's first solve for $\ln K_p$.

$$\ln K_p = \frac{-\Delta G°}{RT}$$

Substituting values gives

$$\ln K_p = \frac{-(-1.40 \times 10^5 \cancel{J} \cancel{mol^{-1}})}{(8.314 \cancel{J} \cancel{mol^{-1}} \cancel{K^{-1}})(298 \cancel{K})}$$
$$= +56.5$$

To calculate K_p, we take the antilogarithm,

$$K_p = e^{56.5}$$
$$= 3 \times 10^{24}$$

Notice that we have expressed the answer to only one significant figure. As discussed earlier, when taking a logarithm, the number of digits written after the decimal place equals the number of significant figures in the number. Conversely, the number of significant figures in the antilogarithm equals the number of digits after the decimal in the logarithm.

Is the Answer Reasonable? The value of $\Delta G°$ is large and negative, so the position of equilibrium should favor the products. The large value of K_p also indicates that the products are favored and, therefore, the result is reasonable.

Practice Exercises

19.25 | The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ has $K_p = 6.9 \times 10^5$ at 25.0 °C. Calculate $\Delta G°$ for this reaction in units of kilojoules. (*Hint*: Be careful with units and significant figures.)

19.26 | The reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ has $\Delta G° = +3.3$ kJ mol^{-1} at 25.0 °C. What is the value of K_p at this temperature?

19.10 | Bond Energies

You have seen how thermodynamic data allow us to predict the spontaneity of chemical reactions as well as the nature of chemical systems at equilibrium. In addition to these useful and important benefits of the study of thermodynamics, there is a bonus. By studying heats of reaction, and heats of formation in particular, we can obtain fundamental information about the chemical bonds in the substances that react. The reasoning is that a chemical reaction results in products that have different bonds than the reactants did. The difference in the total energy of the bonds in the products compared to the total energy of the bonds in the reactants shows up as heat that is lost or gained.

Recall that the **bond energy** is the *amount of energy needed to break a chemical bond to give electrically neutral fragments*. It is a useful quantity to know in the study of chemical properties, because during chemical reactions, bonds within the reactants are broken and new ones are formed as the products appear. The first step—bond breaking—is one of the factors that controls the reactivity of substances. Elemental nitrogen, for example, has a very low degree of reactivity, which is generally attributed to the very strong triple bond in N_2. Reactions that involve the breaking of this bond in a single step simply do not occur. When N_2 does react, it is by a stepwise involvement of its three bonds, one at a time.

- The heats of formation of the nitrogen oxides are endothermic because of the large bond energy of the N_2 molecule.

Determining Bond Energies

The bond energies of simple diatomic molecules such as H_2, O_2, and Cl_2 are usually measured *spectroscopically*. A flame or an electric spark is used to excite (energize) the molecules, causing them to emit light. An analysis of the spectrum of emitted light allows scientists to compute the amount of energy needed to break the bond.

For more complex molecules, thermochemical data can be used to calculate bond energies in a Hess's law kind of calculation. We will use the standard heat of formation of methane to illustrate how this is accomplished. However, before we can attempt such a calculation, we must first define a thermochemical quantity that we will call the **atomization energy**, symbolized $\boldsymbol{\Delta H_{\text{atom}}}$. This is the amount of energy needed to rupture all the chemical bonds in one mole of gaseous molecules to give gaseous atoms as products. For example, the atomization of methane is

$$CH_4(g) \longrightarrow C(g) + 4H(g)$$

and the enthalpy change for the process is ΔH_{atom}. For this particular molecule, ΔH_{atom} corresponds to the total amount of energy needed to break all the C—H bonds in one mole of CH_4; therefore, division of ΔH_{atom} by 4 would give the average C—H bond energy in methane, expressed in kJ mol^{-1}.

■ The kind of bond breaking described here divides the electrons of the bond equally between the two atoms. It could be symbolized as

$$A:B \longrightarrow A^{\cdot} + {}^{\cdot}B$$

Figure 19.18 shows how we can use the standard heat of formation, ΔH_f°, to calculate the atomization energy. Across the bottom we have the chemical equation for the formation of CH_4 from its elements. The enthalpy change for this reaction, of course, is ΔH_f°. In this figure we also can see an alternative three-step path that leads to $CH_4(g)$. One step is the breaking of H—H bonds in the H_2 molecules to give gaseous hydrogen atoms, another is the vaporization of carbon to give gaseous carbon atoms, and the third is the combination of the gaseous atoms to form CH_4 molecules. These changes are labeled 1, 2, and 3 in the figure.

Since $\Delta H = H_{\text{final}} - H_{\text{initial}}$, a difference in state functions, the net enthalpy change from one state to another is the same regardless of the path that we follow. This means that the sum of the enthalpy changes along the upper path must be the same as the enthalpy change along the lower path, ΔH_f°. Perhaps this can be more easily seen in Hess's law terms if we write the changes along the upper path in the form of thermochemical equations.

Steps 1 and 2 have enthalpy changes that are called *standard heats of formation of gaseous atoms.* Values for these quantities have been measured for many of the elements, and some are given in Table 19.3. Step 3 is the opposite of atomization, and

Table 19.3 Standard Heats of Formation of Some Gaseous Atoms from the Elements in Their Standard States

Atom	ΔH_f° per mole of atoms (kJ mol^{-1})[a]
H	217.89
Li	161.5
Be	324.3
B	560
C	716.67
N	472.68
O	249.17
S	276.98
F	79.14
Si	450
P	332.2
Cl	121.47
Br	112.38
I	107.48

[a] All values are positive because forming the gaseous atoms from the elements involves bond breaking and is endothermic.

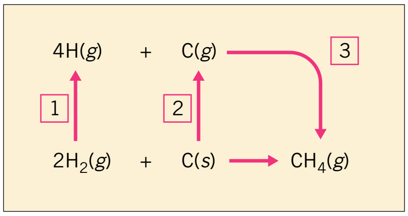


Figure 19.18 | **Two paths for the formation of methane from its elements in their standard states.** As described in the text, steps 1, 2, and 3 of the upper path involve the formation of gaseous atoms of the elements and the formation of bonds in CH_4. The lower path corresponds to the direct combination of the elements in their standard states to give CH_4. Because H is a state function, the sum of the enthalpy changes along the upper path must equal the enthalpy change for the lower path (ΔH_f°).

■ A more complete table of standard heats of formation of gaseous atoms is located in Appendix C.3.

its enthalpy change will therefore be the negative of ΔH_{atom} (recall that if we reverse a reaction, we change the sign of its ΔH).

$$\begin{array}{lrcl}
\text{(Step 1)} & 2\text{H}_2(g) \longrightarrow 4\text{H}(g) & & \Delta H_1^\circ = 4\Delta H^\circ_{\text{f H}(g)} \\
\text{(Step 2)} & \text{C}(s) \longrightarrow \text{C}(g) & & \Delta H_2^\circ = \Delta H^\circ_{\text{f C}(g)} \\
\text{(Step 3)} & 4\text{H}(g) + \text{C}(g) \longrightarrow \text{CH}_4(g) & & \Delta H_3^\circ = -\Delta H_{\text{atom}} \\
\hline
 & 2\text{H}_2(g) + \text{C}(s) \longrightarrow \text{CH}_4(g) & & \Delta H^\circ = \Delta H^\circ_{\text{f CH}_4(g)}
\end{array}$$

Notice that by adding the first three equations, C(g) and 4H(g) cancel and we get the equation for the formation of CH_4 from its elements in their standard states. This means that adding the ΔH° values of the first three equations should give ΔH_f° for CH_4

$$\Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ = \Delta H^\circ_{\text{f CH}_4(g)}$$

Let's substitute for ΔH_1°, ΔH_2°, and ΔH_3°, and then solve for ΔH_{atom}. First, we substitute for the ΔH° quantities:

$$4\Delta H^\circ_{\text{f H}(g)} + \Delta H^\circ_{\text{f C}(g)} + (-\Delta H_{\text{atom}}) = \Delta H^\circ_{\text{f CH}_4(g)}$$

Next, we solve for ($-\ \Delta H_{\text{atom}}$):

$$-\Delta H_{\text{atom}} = \Delta H^\circ_{\text{f CH}_4(g)} - 4\Delta H^\circ_{\text{f H}(g)} - \Delta H^\circ_{\text{f C}(g)}$$

Changing signs and rearranging the right side of the equation just a bit gives

$$\Delta H_{\text{atom}} = 4\Delta H^\circ_{\text{f H}(g)} + \Delta H^\circ_{\text{f C}(g)} - \Delta H^\circ_{\text{f CH}_4(g)}$$

Now all we need are the ΔH_f° values for the substances indicated on the right side. From Table 19.3 we obtain $\Delta H^\circ_{\text{f H}(g)}$ and $\Delta H^\circ_{\text{f C}(g)}$, and the value of $\Delta H^\circ_{\text{f CH}_4(g)}$ is obtained from Table 7.2. We will round these to the nearest 0.1 kJ/mol.

$$\begin{aligned}
\Delta H^\circ_{\text{f H}(g)} &= +217.9 \text{ kJ/mol} \\
\Delta H^\circ_{\text{f C}(g)} &= +716.7 \text{ kJ/mol} \\
\Delta H^\circ_{\text{f CH}_4(g)} &= -74.8 \text{ kJ/mol}
\end{aligned}$$

Substituting these values gives

$$\Delta H_{\text{atom}} = 1663.1 \text{ kJ/mol}$$

and division by 4 gives an estimate of the average C—H bond energy in this molecule.

$$\begin{aligned}
\text{Bond energy} &= \frac{1663.1 \text{ kJ/mol}}{4} \\
&= 415.8 \text{ kJ/mol of C—H bonds}
\end{aligned}$$

This value is quite close to the one in Table 19.4, which is an average of the C—H bond energies in many different compounds. The other bond energies in Table 19.4 are also based on thermochemical data and were obtained by similar calculations.

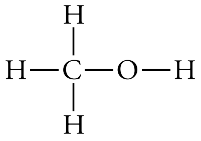
Table 19.4 Some Average Bond Energies

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
C—C	348	C—Br	276
C═C	612	C—I	238
C≡C	960	H—H	436
C—H	412	H—F	565
C—N	305	H—Cl	431
C═N	613	H—Br	366
C≡N	890	H—I	299
C—O	360	H—N	388
C═O	743	H—O	463
C—F	484	H—S	338
C—Cl	338	H—Si	376

Estimating Heats of Formation

An amazing thing about many covalent bond energies is that they are very nearly the same in many different compounds. This suggests, for example, that a C—H bond is very nearly the same in CH_4 as it is in C_3H_6 or $C_{15}H_{32}$ or a large number of other compounds that contain this kind of bond.

Because the bond energy doesn't vary much from compound to compound, we can use tabulated bond energies to estimate the heats of formation of substances. For example, let's calculate the standard heat of formation of methyl alcohol vapor, $CH_3OH(g)$. The structural formula for methanol is



$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \\ \text{H} \end{array}$$

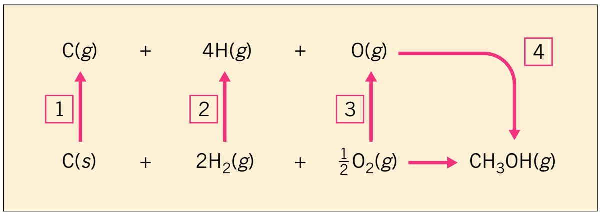


Figure 19.19 | **Two paths for the formation of methyl alcohol vapor from its elements in their standard states.** The numbered paths are discussed in the text.

To perform this calculation, we set up two paths from the elements to the compound, as shown in Figure 19.19. The lower path has an enthalpy change corresponding to $\Delta H^\circ_{\text{f}\,CH_3OH(g)}$, while the upper path takes us to the gaseous elements and then through the energy released when the bonds in the molecule are formed. This latter energy can be computed from the bond energies in Table 19.4. As before, the sum of the energy changes along the upper path must be the same as the energy change along the lower path, and this permits us to compute $\Delta H^\circ_{\text{f}\,CH_3OH(g)}$.

Steps 1, 2, and 3 involve the formation of the gaseous atoms from the elements, and their enthalpy changes are obtained from Table 19.3.

$$\Delta H^\circ_1 = \Delta H^\circ_{\text{f}\,C(g)} = 1 \text{ mol} \times 716.7 \text{ kJ/mol} = 716.7 \text{ kJ}$$

$$\Delta H^\circ_2 = 4\Delta H^\circ_{\text{f}\,H(g)} = 4 \text{ mol} \times (217.9 \text{ kJ/mol}) = 871.6 \text{ kJ}$$

$$\Delta H^\circ_3 = \Delta H^\circ_{\text{f}\,O(g)} = 1 \text{ mol} \times (249.2 \text{ kJ/mol}) = 249.2 \text{ kJ}$$

The sum of these values, +1837.5 kJ, is the total energy-input (the net ΔH°) for the first three steps.

The formation of the CH_3OH molecule from the gaseous atoms is exothermic because *energy is always released* when atoms become joined by covalent bonds. In this molecule we can count three C—H bonds, one C—O bond, and one O—H bond. Their formation releases energy equal to their bond energies, which we obtain from Table 19.4.

Bond	Energy (kJ)
3(C—H)	3 × (412 kJ/mol) = 1236
C—O	360
O—H	463

Adding these together gives a total of 2059 kJ. Therefore, for Step 4 in Figure 19.19 the enthalpy, ΔH°_4, is −2059 kJ (because bond formation is exothermic). Now we can compute the total enthalpy change for the upper path.

$$\begin{aligned} \Delta H^\circ &= (+1837.5 \text{ kJ}) + (-2059 \text{ kJ}) \\ &= -222 \text{ kJ} \end{aligned}$$

The value just calculated should be equal to ΔH°_f for $CH_3OH(g)$. For comparison, it has been found experimentally that ΔH°_f for this molecule (in the vapor state) is −201 kJ/mol. At first glance, the agreement doesn't seem very good, but on a relative basis the calculated value (−222 kJ) differs from the experimental one by only about 10%.

Practice Exercises

19.27 | Determine the heat of formation of gaseous 1-propanol ($CH_3CH_2CH_2OH$) and 2-bromobutane ($CH_3CHBrCH_2CH_3$). (*Hint*: Remember that bond formation is exothermic.)

19.28 | Determine the heat of formation of gaseous cyclohexane, C_6H_{12}. Cyclohexane is a six-member carbon ring with two hydrogen atoms attached to each carbon atom. Do the same for benzene, C_6H_6. (See Section 9.9, page 397 for the structure.)

Summary

First Law of Thermodynamics. The change in the **internal energy** of a system, ΔE, equals the sum of the heat absorbed by the system, q, and the work done on the system, w. ΔE does not depend on the path from E_{initial} to E_{final}, whereas q and w do depend on the path taken. For pressure–volume work, $w = -P\,\Delta V$, where P is the external pressure and $\Delta V = V_{\text{final}} - V_{\text{initial}}$. The heat at constant volume, q_v, is equal to ΔE, whereas the heat at constant pressure, q_p, is equal to ΔH. The value of ΔH differs from ΔE by the work expended in pushing back the atmosphere when the change occurs at constant atmospheric pressure. In general, the difference between ΔE and ΔH is quite small. For a chemical reaction, $\Delta H = \Delta E + \Delta n_{\text{gas}} RT$, where Δn_{gas} is the change in the number of moles of gas when going from reactants to products.

Spontaneity. A **spontaneous change** occurs without outside assistance, whereas a nonspontaneous changes requires continuous help and can occur only if it is accompanied by and linked to some other spontaneous event.

Spontaneity is associated with statistical probability—spontaneous processes tend to proceed from lower probability states to those of higher probability. The thermodynamic quantity associated with the probability of a state is **entropy, *S*.** Entropy is a state function that is a measure of the number of energetically equivalent ways, microstates, W, a state can be realized. In general, gases have much higher entropies than liquids, which have somewhat higher entropies than solids. Entropy increases with volume for a gas and with the temperature. During a chemical reaction, the entropy tends to increase if the number of molecules increases.

Second Law of Thermodynamics. This law states that the entropy of the universe (system plus surroundings) increases whenever a spontaneous change occurs.

Gibbs Free Energy. The **Gibbs free energy**, G, is a state function and its change, ΔG, allows us to determine the combined effects of enthalpy and entropy changes on the spontaneity of a chemical or physical change. A change is spontaneous only if the free energy of the system decreases (ΔG is negative). When ΔH and ΔS have the same algebraic sign, the temperature becomes the critical factor in determining spontaneity.

Third Law of Thermodynamics. The entropy of a pure crystalline substance is equal to zero at absolute zero (0 K). Standard entropies, $S°$, are calculated for 25 °C and 1 atm (Table 19.1) and can be used to calculate $\Delta S°$ for chemical reactions.

Standard Free Energy Changes. When ΔG is measured at 25 °C and 1 atm, it is the **standard free energy change, $\Delta G°$. Standard free energies of formation,** ΔG_f°, can be used to obtain $\Delta G°$ for chemical reactions by a Hess's law type of calculation.

For any system, the value of ΔG is equal to the maximum amount of energy that can be obtained in the form of useful work, which can be obtained only if the change takes place by a **reversible process.** All real changes are irreversible and we always obtain less work than is theoretically available; the rest is lost as heat.

Free Energy and Equilibrium. When a system reaches equilibrium, $\Delta G = 0$ and no useful work can be obtained from it. For a phase change (e.g., solid $\rightleftharpoons$ liquid) ΔS and ΔH are related by the equation $\Delta S = \Delta H/T$, where T is the temperature at which the two phases are in equilibrium.

In chemical reactions, equilibrium occurs at a minimum on the free energy curve part way between pure reactants and pure products. The composition of the equilibrium mixture is determined by where the minimum lies along the reactant $\longrightarrow$ product axis; when it lies close to the products, the proportion of product to reactants is large and the reaction goes far toward completion.

When a reaction has a value of $\Delta G°$ that is both large and negative, it will appear to occur spontaneously because a lot of products will be formed by the time equilibrium is reached. If $\Delta G°$ is large and positive, it may be difficult to observe any reaction at all because only tiny amounts of products will be formed.

Thermodynamic Equilibrium Constants. The spontaneity of a reaction is determined by ΔG (how the free energy changes with a change in concentration). This is related to the standard free energy change, $\Delta G°$, by the equation $\Delta G = \Delta G° + RT \ln Q$, where Q is the reaction quotient for the system. At equilibrium, $\Delta G° = -RT \ln K$, where $K = K_p$ for gaseous reactions and $K = K_c$ for reactions in solution.

Bond Energies and Heats of Reaction. The **bond energy** equals the amount of energy needed to break a bond to give neutral fragments. The sum of all the bond energies in a molecule is the **atomization energy, ΔH_{atom},** and, on a mole basis, it corresponds to the energy needed to break one mole of molecules into individual atoms. The heat of formation of a gaseous compound equals the sum of the energies needed to form atoms of the elements that are found in the substance plus the negative of the atomization energy.

Tools for Problem Solving

In this chapter you learned to apply the following concepts as tools in solving problems related to thermodynamics. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution.

Converting between ΔE and ΔH (page 873)

Use the following equation when you need to find the difference between ΔE and ΔH, or when converting from one to the other.

$$\Delta H = \Delta E + \Delta n_{\text{gas}} RT$$

Use the coefficients of gaseous reactants and products to calculate Δn_{gas}.

Factors that affect the entropy (pages 877 through 879)

You can sometimes anticipate the sign of the entropy change for a system because certain factors favor an increase in entropy.

- *Volume*: Entropy increases with increasing volume.
- *Temperature*: Entropy increases with increasing temperature.
- *Physical state*: $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$. When gases are formed in a reaction, ΔS is almost always positive.
- *Number of particles*: Entropy increases when the number of particles increases.

Gibbs free energy (page 882)

The Gibbs free energy is defined in terms of ΔH and ΔS by the equation

$$\Delta G = \Delta H - T\Delta S$$

ΔG as a predictor of spontaneity (page 882)

You can use the sign of ΔG to tell whether a particular change is spontaneous.

Standard entropy change (page 884)

Calculate the standard entropy change for a reaction using the following equation and standard entropy values from Table 19.1. The calculation is similar to the Hess's law calculation of ΔH° you learned in Chapter 7.

$$\Delta S^\circ = (\text{sum of } S^\circ \text{ of products}) - (\text{sum of } S^\circ \text{ of reactants})$$

Calculating ΔG° from ΔH° and ΔS° (page 887)

By calculating ΔH° from data in Table 7.2 and ΔS° from data in Table 19.1 you can calculate ΔG° for a reaction. The equation is

$$\Delta G^\circ = \Delta H^\circ - (298.15\text{ K})\,\Delta S^\circ$$

Calculating ΔG° using ΔG_f° values (page 888)

When you want ΔG° for a reaction, use ΔG_f° data from Table 19.2 and the equation

$$\Delta G^\circ = (\text{sum of } \Delta G_f^\circ \text{ of products}) - (\text{sum of } \Delta G_f^\circ \text{ of reactants})$$

Using ΔG° to assess the position of equilibrium (page 897)

The sign and magnitude can serve as a qualitative indicator of the position of equilibrium and lets us anticipate whether an observable amount of product will be formed in a reaction.

- ΔG° is large and positive: position of equilibrium is close to reactants.
- ΔG° is large and negative: position of equilibrium is close to products.
- $\Delta G^\circ = 0$: position of equilibrium lies about midway between reactants and products.

Calculating $\Delta G°$ at temperatures other than 25 °C (page 898)

When you need $\Delta G°$ at some temperature other than 25 °C, assume $\Delta H°$ and $\Delta S°$ are nearly independent of temperature and use the equation

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ$$

Such a calculation would be needed to estimate an equilibrium constant at a temperature other than 25 °C.

Relating the reaction quotient to ΔG (page 900)

We can tell whether a particular reaction mixture composition will lead to a spontaneous reaction in the forward direction, the reverse direction, or whether the reaction is at equilibrium by calculating ΔG by the equation

$$\Delta G = \Delta G° + RT \ln Q$$

- If ΔG is negative, the reaction is spontaneous in the forward direction.
- If ΔG is positive, the reaction is spontaneous in the reverse direction.
- If ΔG is zero, the reaction is at equilibrium.

Determining thermodynamic equilibrium constants (page 902)

The following important equation lets us calculate equilibrium constants from thermodynamic data, or calculate $\Delta G°$ from measured equilibrium constants.

$$\Delta G° = -RT \ln K$$

Remember to use $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T in kelvins, and that $K = K_P$ for gaseous reactions and K_c for reactions in solution.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

First Law of Thermodynamics

19.1 What is the origin of the name *thermodynamics*?

19.2 State the first law of thermodynamics in words. What equation defines the change in the internal energy in terms of heat and work? Define the meaning of the symbols, including the significance of their algebraic signs.

19.3 How is a change in the internal energy defined in terms of the initial and final internal energies?

19.4 What is the algebraic sign of ΔE for an endothermic change? Why?

19.5 Which quantities in the statement of the first law are state functions and which are not?

19.6 Which thermodynamic quantity corresponds to the heat at constant volume? Which corresponds to the heat at constant pressure?

19.7 What are the units of $P\Delta V$ if pressure is expressed in pascals and volume is expressed in cubic meters?

19.8 If there is a decrease in the number of moles of gas during an exothermic chemical reaction, which is numerically larger, ΔE or ΔH? Why?

19.9 Which of the following changes is accompanied by the most negative value of ΔE? (a) A spring is compressed and heated. (b) A compressed spring expands and is cooled. (c) A spring is compressed and cooled. (d) A compressed spring expands and is heated.

Spontaneous Change

19.10 What is a *spontaneous change*? What role does kinetics play in determining the apparent spontaneity of a chemical reaction?

19.11 List five changes that you have encountered recently that occurred spontaneously. List five changes that are nonspontaneous that you have caused to occur.

19.12 Which of the items that you listed in Question 19.11 are exothermic (leading to a lowering of the potential energy) and which are endothermic (accompanied by an increase in potential energy)?

19.13 At constant pressure, what role does the enthalpy change play in determining the spontaneity of an event?

19.14 How do the probabilities of the initial and final states in a process affect the spontaneity of the process?

Entropy

19.15 An instant cold pack purchased in a pharmacy contains a packet of solid ammonium nitrate surrounded by a pouch of water. When the packet of NH_4NO_3 is broken, the solid dissolves in water and a cooling of the mixture occurs because the solution process for NH_4NO_3 in water is endothermic. Explain, in terms of what happens to the molecules and ions, why this mixing occurs spontaneously.

19.16 What is *entropy*?

19.17 How is the entropy of a substance affected by (a) an increase in temperature, (b) a decrease in volume, (c) changing from a liquid to a solid, and (d) dissociating into individual atoms?

19.18 Will the entropy change for each of the following be positive or negative?

(a) Moisture condenses on the outside of a cold glass.

(b) Raindrops form in a cloud.

(c) Gasoline vaporizes in the carburetor of an automobile engine.

(d) Air is pumped into a tire.

(e) Frost forms on the windshield of your car.

(f) Sugar dissolves in coffee.

19.19 On the basis of our definition of entropy, suggest why entropy is a state function.

19.20 State the second law of thermodynamics.

19.21 How can a process have a negative entropy change for the system, and yet still be spontaneous?

Third Law of Thermodynamics and Standard Entropies

19.22 What is the third law of thermodynamics?

19.23 Would you expect the entropy of an alloy (a solution of two metals) to be zero at 0 K? Explain your answer.

19.24 Why does entropy increase with increasing temperature?

19.25 Does glass have $S = 0$ at 0 K? Explain.

Standard (Gibbs) Free Energy Change, $\Delta G°$

19.26 What is the equation expressing the change in the Gibbs free energy for a reaction occurring at constant temperature and pressure?

19.27 In terms of the algebraic signs of ΔH and ΔS, under which of the following circumstances will a change be spontaneous:

(a) At all temperatures?

(b) At low temperatures but not at high temperatures?

(c) At high temperatures but not at low temperatures?

19.28 Under what circumstances will a change be nonspontaneous regardless of the temperature?

Maximum Work and ΔG

19.29 How is free energy related to useful work?

19.30 What is a thermodynamically reversible process? How is the amount of work obtained from a change related to thermodynamic reversibility?

19.31 How is the *rate* at which energy is withdrawn from a system related to the amount of that energy that can appear as useful work?

19.32 When glucose is oxidized by the body to generate energy, part of the energy is used to make molecules of ATP (adenosine triphosphate). However, of the total energy released in the oxidation of glucose, only 38% actually goes to making ATP. What happens to the rest of the energy?

19.33 Why are real, observable changes not considered to be thermodynamically reversible processes?

Free Energy and Equilibrium

19.34 In what way is free energy related to equilibrium?

19.35 Considering the fact that the formation of a bond between two atoms is exothermic and is accompanied by an entropy decrease, explain why all chemical compounds decompose into individual atoms if heated to a high enough temperature.

19.36 When a warm object is placed in contact with a cold one, they both gradually come to the same temperature. On a molecular level, explain how this is related to entropy and spontaneity.

19.37 Sketch the shape of the free energy curve for a chemical reaction that has a positive $\Delta G°$. Indicate the composition of the reaction mixture corresponding to equilibrium.

19.38 Many reactions that have large, negative values of $\Delta G°$ are not actually observed to happen at 25 °C and 1 atm. Why?

Standard Free Energy and Equilibrium Constants

19.39 Suppose a reaction has a negative $\Delta H°$ and a negative $\Delta S°$. Will more or less product be present at equilibrium as the temperature is raised?

19.40 Write the equation that relates the free energy change to the value of the reaction quotient for a reaction.

19.41 How is the equilibrium constant related to the standard free energy change for a reaction? (Write the equation.)

19.42 What is the value of $\Delta G°$ for a reaction for which $K = 1$?

Bond Energies and Heats of Reaction

19.43 Define the term atomization energy.

19.44 Why are the heats of formation of gaseous atoms from their elements endothermic quantities?

19.45 The gaseous C_2 molecule has a bond energy of 602 kJ mol^{-1}. Why isn't the standard heat of formation of C(g) equal to half this value?

Review Problems

First Law of Thermodynamics

19.46 A certain system absorbs 0.300 kJ of heat and has 0.700 kJ of work performed on it. What is the value of ΔE for the change? Is the overall change exothermic or endothermic?

19.47 The value of ΔE for a certain change is -1455 J. During the change, the system absorbs 812 J of heat. Did the system do work, or was work done on the system? How much work, expressed in joules, was involved?

19.48 Suppose that you were pumping an automobile tire with a hand pump that pushed 24.0 in.^{3} of air into the tire on each stroke, and that during one such stroke the opposing pressure in the tire was 30.0 lb/in.^{2} above the normal atmospheric pressure of 14.7 lb/in.^{2}. Calculate the number of joules of work accomplished during each stroke. (1 L atm = 101.325 J)

OH **19.49** Consider the reaction between aqueous solutions of baking soda, $NaHCO_3$, and vinegar, $HC_2H_3O_2$.

$$NaHCO_3(aq) + HC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

If this reaction occurs at 1.00 atmospheres of pressure, how much work, expressed in *L atm*, is done by the system in pushing back the atmosphere when 1.00 mol $NaHCO_3$ reacts at a temperature of 25 °C? (*Hint*: Review the gas laws.)

19.50 Calculate $\Delta H°$ and $\Delta E°$ for the following reactions at 25 °C. (If necessary, refer to the data in Table C.2 in Appendix C.)

(a) $3PbO(s) + 2NH_3(g) \longrightarrow 3Pb(s) + N_2(g) + 3H_2O(g)$

(b) $NaOH(s) + HCl(g) \longrightarrow NaCl(s) + H_2O(l)$

(c) $Al_2O_3(s) + 2Fe(s) \longrightarrow Fe_2O_3(s) + 2Al(s)$

(d) $2CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$

19.51 Calculate $\Delta H°$ and $\Delta E°$ for the following reactions at 25 °C. (If necessary, refer to the data in Table C.2 in Appendix C.)

(a) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$

(b) $C_2H_2(g) + 5N_2O(g) \longrightarrow 2CO_2(g) + H_2O(g) + 5N_2(g)$

(c) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$

(d) $(CH_3)_2CO(l) + 4O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(g)$

19.52 The reaction

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

has $\Delta H° = -163.14$ kJ. What is the value of ΔE for the decomposition of 186 g of N_2O at 25 °C? If we assume that ΔH doesn't change appreciably with temperature, what is ΔE for this same reaction at 217 °C?

19.53 A 10.0 L vessel at 22 °C contains butane, $C_4H_{10}(g)$, at a pressure of 2.00 atm. What is the maximum amount of work that can be obtained by the combustion of this butane if the gas is first brought to a pressure of 1 atm and the temperature is brought to 28 °C? Assume the products are also returned to this same temperature and pressure.

Spontaneous Chemical and Physical Change

19.54 Use the data from Table 7.2 to calculate $\Delta H°$ for the following reactions. On the basis of their values of $\Delta H°$, which are favored to occur spontaneously?

(a) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

(b) $C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$

(c) $3CaO(s) + 2Fe(s) \longrightarrow 3Ca(s) + Fe_2O_3(s)$

19.55 Use the data from Table 7.2 to calculate $\Delta H°$ for the following reactions. On the basis of their values of $\Delta H°$, which are favored to occur spontaneously?

(a) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$

(b) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$

(c) $C_2H_2(g) + 5N_2O(g) \longrightarrow 2CO_2(g) + H_2O(g) + 5N_2(g)$

19.56 What factors must you consider to determine the sign of ΔS for the reaction $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$ if it occurs at constant temperature?

19.57 What factors must you consider to determine the sign of ΔS for the reaction: $2HI(g) \longrightarrow H_2(g) + I_2(s)$?

19.58 Predict the algebraic sign of the entropy change for the following reactions.

(a) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$

(b) $SO_2(g) + CaO(s) \longrightarrow CaSO_3(s)$

(c) $CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$

(d) $Ni(s) + 2HCl(aq) \longrightarrow H_2(g) + NiCl_2(aq)$

OH **19.59** Predict the algebraic sign of the entropy change for the following reactions.

(a) $I_2(s) \longrightarrow I_2(g)$

(b) $Br_2(g) + 3Cl_2(g) \longrightarrow 2BrCl_3(g)$

(c) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

(d) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$

Third Law of Thermodynamics

19.60 Calculate $\Delta S°$ for the following reactions in J K^{-1} from the data in Table 19.1. On the basis of their values of $\Delta S°$, which of these reactions are favored to occur spontaneously?

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(b) $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$

(c) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$

(d) $Ca(OH)_2(s) + H_2SO_4(l) \longrightarrow CaSO_4(s) + 2H_2O(l)$

(e) $S(s) + 2N_2O(g) \longrightarrow SO_2(g) + 2N_2(g)$

19.61 Calculate $\Delta S°$ for the following reactions in J K^{-1}, using the data in Table 19.1.

(a) $Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s)$

(b) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

(d) $CaCO_3(s) + H_2SO_4(l) \longrightarrow CaSO_4(s) + H_2O(g) + CO_2(g)$

(e) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

OH **19.62** Calculate $\Delta S_f°$ for the following compounds in J mol^{-1} K^{-1}.

(a) $C_2H_4(g)$

(b) $HC_2H_3O_2(l)$

(c) $CaSO_4 \cdot 2H_2O(s)$

19.63 Calculate $\Delta S_f°$ for the following compounds in J mol^{-1} K^{-1}.

(a) $Al_2O_3(s)$

(b) $CaSO_4 \cdot \frac{1}{2}H_2O(s)$

(c) $NH_4Cl(s)$

19.64 Nitrogen dioxide, NO_2, an air pollutant, dissolves in rainwater to form a dilute solution of nitric acid. The equation for the reaction is

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(l) + NO(g)$$

Calculate $\Delta S°$ for this reaction in J K^{-1}.

19.65 Good wine will turn to vinegar if it is left exposed to air, because the alcohol is oxidized to acetic acid. The equation for the reaction is

$$C_2H_5OH(l) + O_2(g) \longrightarrow HC_2H_3O_2(l) + H_2O(l)$$

Calculate $\Delta S°$ for this reaction in J K^{-1}.

Standard (Gibbs) Free Energy

ILW **19.66** Phosgene, $COCl_2$, was used as a war gas during World War I. It reacts with the moisture in the lungs to produce HCl, which causes the lungs to fill with fluid, and CO, which asphyxiates the victim. Both lead ultimately to death. For $COCl_2(g)$, $S° = 284$ J/mol K and $\Delta H_f° = -223$ kJ/mol. Use this information and the data in Table 19.1 to calculate $\Delta G_f°$ for $COCl_2(g)$ in kJ mol^{-1}.

OH **19.67** Aluminum oxidizes rather easily, but forms a thin protective coating of Al_2O_3 that prevents further oxidation of the aluminum beneath. Use the data for $\Delta H_f°$ (Table 7.2) and $S°$ (Table 19.1) to calculate $\Delta G_f°$ for $Al_2O_3(s)$ in kJ mol^{-1}.

19.68 Compute $\Delta G°$ in kJ for the following reactions, using the data in Table 19.2.

(a) $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$

(b) $2NH_4Cl(s) + CaO(s) \longrightarrow CaCl_2(s) + H_2O(l) + 2NH_3(g)$

(c) $CaSO_4(s) + 2HCl(g) \longrightarrow CaCl_2(s) + H_2SO_4(l)$

19.69 Compute $\Delta G°$ in kJ for the following reactions, using the data in Table 19.2.

(a) $2HCl(g) + CaO(s) \longrightarrow CaCl_2(s) + H_2O(g)$

(b) $2AgCl(s) + Ca(s) \longrightarrow CaCl_2(s) + 2Ag(s)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(l) + NO(g)$

***19.70** Given the following,

$$4NO(g) \longrightarrow 2N_2O(g) + O_2(g) \qquad \Delta G° = -139.56 \text{ kJ}$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta G° = -69.70 \text{ kJ}$$

calculate $\Delta G°$ for the reaction

$$2N_2O(g) + 3O_2(g) \longrightarrow 4NO_2(g)$$

***19.71** Given the following reactions and their $\Delta G°$ values,

$$COCl_2(g) + 4NH_3(g) \longrightarrow CO(NH_2)_2(s) + 2NH_4Cl(s) \qquad \Delta G° = -332.0 \text{ kJ}$$

$$COCl_2(g) + H_2O(l) \longrightarrow CO_2(g) + 2HCl(g) \qquad \Delta G° = -141.8 \text{ kJ}$$

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta G° = -91.96 \text{ kJ}$$

Calculate the value of $\Delta G°$ for the reaction

$$CO(NH_2)_2(s) + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

Free Energy and Work

OH **19.72** Gasohol is a mixture of gasoline and ethanol (grain alcohol), C_2H_5OH. Calculate the maximum work that could be obtained at 25 °C and 1 atm by burning 1 mol of C_2H_5OH.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

19.73 What is the maximum amount of useful work that could possibly be obtained at 25 °C and 1 atm from the combustion of 48.0 g of natural gas, $CH_4(g)$ to give $CO_2(g)$ and $H_2O(g)$?

Free Energy and Equilibrium

19.74 Chloroform, formerly used as an anesthetic and now believed to be a carcinogen, has a heat of vaporization $\Delta H_{\text{vaporization}} = 31.4$ kJ mol^{-1}. The change, $CHCl_3(l) \longrightarrow CHCl_3(g)$, has $\Delta S° = 94.2$ J mol^{-1} K^{-1}. At what temperature do we expect $CHCl_3$ to boil (i.e., at what temperature will liquid and vapor be in equilibrium at 1 atm pressure)?

OH **19.75** For the melting of aluminum, $Al(s) \longrightarrow Al(l)$, $\Delta H° = 10.0$ kJ mol^{-1} and $\Delta S° = 9.50$ J/mol K. Calculate the melting point of Al. (The actual melting point is 660 °C.)

19.76 Isooctane, an important constituent of gasoline, has a boiling point of 99.3 °C and a heat of vaporization of 37.7 kJ mol^{-1}. What is ΔS (in J mol^{-1} K^{-1}) for the vaporization of 1 mol of isooctane?

19.77 Acetone (nail polish remover) has a boiling point of 56.2 °C. The change, $(CH_3)_2CO(l) \longrightarrow (CH_3)_2CO(g)$, has $\Delta H° = 31.9$ kJ mol^{-1}. What is $\Delta S°$ for this change?

Free Energy and Spontaneity of Chemical Reactions

ILW **19.78** Determine whether the following reaction (equation unbalanced) will be spontaneous at 25 °C. (Do we expect appreciable amounts of products to form?)

$$C_2H_4(g) + HNO_3(l) \longrightarrow HC_2H_3O_2(l) + H_2O(l) + NO(g) + NO_2(g)$$

19.79 Which of the following reactions (equations unbalanced) would be expected to be spontaneous at 25 °C and 1 atm?

(a) $PbO(s) + NH_3(g) \longrightarrow Pb(s) + N_2(g) + H_2O(g)$

(b) $NaOH(s) + HCl(g) \longrightarrow NaCl(s) + H_2O(l)$

(c) $Al_2O_3(s) + Fe(s) \longrightarrow Fe_2O_3(s) + Al(s)$

(d) $2CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$

Thermodynamic Equilibrium Constants

OH **19.80** Calculate the value of the thermodynamic equilibrium constant for the following reactions at 25 °C. (Refer to the data in Appendix C.2.)

(a) $2PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

19.81 Calculate the value of the thermodynamic equilibrium constant for the following reactions at 25 °C. (Refer to the data in Appendix C.2.)

(a) $N_2H_4(g) + 2O_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$

(b) $N_2H_4(g) + 6H_2O_2(g) \rightleftharpoons 2NO_2(g) + 8H_2O(g)$

ILW **19.82** The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ has $\Delta G^\circ_{1273} = -9.67$ kJ. A 1.00 L reaction vessel at 1000.0 °C contains 0.0200 mol NO_2, 0.040 mol NO, 0.015 mol N_2O, and 0.0350 mol O_2. Is the reaction at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium?

19.83 The reaction $CO(g) + H_2O(g) \rightleftharpoons HCHO_2(g)$ has $\Delta G^\circ_{673} = +79.8$ kJ mol^{-1}. If a mixture at 673 K contains 0.040 mol CO, 0.022 mol H_2O, and 3.8×10^{-3} mol $HCHO_2$ in a 2.50 L container, is the reaction at equilibrium? If not, in which direction will the reaction proceed spontaneously?

19.84 A reaction that can convert coal to methane (the chief component of natural gas) is

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

for which $\Delta G^\circ = -50.79$ kJ mol^{-1}. What is the value of K_p for this reaction at 25 °C? Does this value of K_p suggest that studying this reaction as a means of methane production is worthwhile pursuing?

***19.85** One of the important reactions in living cells from which the organism draws energy is the reaction of adenosine triphosphate (ATP) with water to give adenosine diphosphate (ADP) and free phosphate ion.

$$ATP + H_2O \rightleftharpoons ADP + PO_4^{3-}$$

The value of ΔG°_{310} for this reaction at 37 °C (normal human body temperature) is -33 kJ mol^{-1}. Calculate the value of the equilibrium constant for the reaction at this temperature.

19.86 What is the value of the equilibrium constant for a reaction for which $\Delta G^\circ = 0$? What will happen to the composition of the system if we begin the reaction with the pure products?

19.87 Methanol, a potential replacement for gasoline as an automotive fuel, can be made from H_2 and CO by the reaction

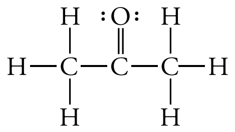
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At 500.0 K, this reaction has $K_p = 6.25 \times 10^{-3}$. Calculate ΔG°_{500} for this reaction in units of kilojoules.

Bond Energies

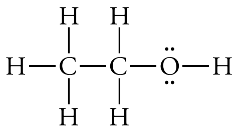
19.88 Use the data in Table 19.4 to compute the approximate atomization energy of NH_3.

19.89 Approximately how much energy would be released during the formation of the bonds in one mole of acetone molecules? Acetone, the solvent usually found in nail polish remover, has the structural formula



$$\begin{array}{ccccccccc} & & H & & :\!O\!: & & H & & \\ & & | & & \| & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

OH **19.90** The standard heat of formation of ethanol vapor, $C_2H_5OH(g)$, is -235.3 kJ mol^{-1}. Use the data in Table 19.3 and the average bond energies for C—C, C—H, and O—H bonds to estimate the C—O bond energy in this molecule. The structure of the molecule is



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & \ddot{\underset{..}{O}} & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

19.91 The standard heat of formation of ethylene, $C_2H_4(g)$, is $+52.284$ kJ mol^{-1}. Calculate the C═C bond energy in this molecule.

ILW **19.92** Carbon disulfide, CS_2, has the Lewis structure $:\ddot{S}=C=\ddot{S}:$, and for $CS_2(g)$, $\Delta H^\circ_f = +115.3$ kJ mol^{-1}. Use the data in Table 19.3 to calculate the average C═S bond energy in this molecule.

19.93 Gaseous hydrogen sulfide, H_2S, has $\Delta H^\circ_f = -20.15$ kJ mol^{-1}. Use the data in Table 19.3 to calculate the average S—H bond energy in this molecule.

19.94 For $SF_6(g)$, $\Delta H^\circ_f = -1096$ kJ mol^{-1}. Use the data in Table 19.3 to calculate the average S—F bond energy in SF_6.

19.95 Use the results of the preceding problem and the data in Table C.3 of Appendix C to calculate the standard heat of formation of $SF_4(g)$. The measured value of ΔH_f° for $SF_4(g)$ is -718.4 kJ mol^{-1}. What is the percentage difference between your calculated value of ΔH_f° and the experimentally determined value?

19.96 Use the data in Tables 19.3 and 19.4 to estimate the standard heat of formation of acetylene, $H—C \equiv C—H$, in the gaseous state.

19.97 What would be the approximate heat of formation of CCl_4 vapor at 25 °C and 1 atm?

19.98 Which substance should have the more exothermic heat of formation, CF_4 or CCl_4?

***19.99** Would you expect the value of ΔH_f° for benzene, C_6H_6, computed from tabulated bond energies, to be very close to the experimentally measured value of ΔH_f°? Justify your answer.

Additional Exercises

19.100 If pressure is expressed in atmospheres and volume is expressed in liters, $P\,\Delta V$ has units of L atm (liters × atmospheres). In Chapter 11 you learned that 1 atm = 101,325 Pa, and in Chapter 2 you learned that 1 L = 1 dm^3. Use this information to determine the number of joules corresponding to 1 L atm.

19.101 Calculate the work, in joules, done by a gas as it expands at constant temperature from a volume of 3.00 L and a pressure of 5.00 atm to a volume of 8.00 L. The external pressure against which the gas expands is 1.00 atm. (1 atm = 101,325 Pa)

***19.102** When an ideal gas expands at a constant temperature, $\Delta E = 0$ for the change. Why?

***19.103** When a real gas expands at a constant temperature, $\Delta E > 0$ for the change. Why?

19.104 An ideal gas in a cylinder fitted with a piston expands at constant temperature from a pressure of 5 atm and a volume of 6.0 L to a final volume of 12 L against a constant opposing pressure of 2.5 atm. How much heat does the gas absorb, expressed in units of L atm (liter × atm)? (*Hint*: See Exercise 19.102.)

***19.105** A cylinder fitted with a piston contains 5.00 L of a gas at a pressure of 4.00 atm. The entire apparatus is contained in a water bath to maintain a constant temperature of 25 °C. The piston is released and the gas expands until the pressure inside the cylinder equals the atmospheric pressure outside, which is 1 atm. Assume ideal gas behavior and calculate the amount of work done by the gas as it expands at constant temperature.

***19.106** The experiment described in Exercise 19.105 is repeated, but this time a weight, which exerts a pressure of 2 atm, is placed on the piston. When the gas expands, its pressure drops to this 2 atm pressure. Then the weight is removed and the gas is allowed to expand again to a final pressure of 1 atm. Throughout both expansions the temperature of the apparatus was held at a constant 25 °C. Calculate the amount of work performed by the gas in each step. How does the combined total amount of work in this two-step expansion compare with the amount of work done by the gas in the one-step expansion described in Exercise 19.105? How can even more work be obtained by the expansion of the gas?

19.107 When potassium iodide dissolves in water, the mixture becomes cool. For this change, which is of a larger magnitude, $T\,\Delta S$ or ΔH?

19.108 The enthalpy of combustion, $\Delta H^\circ_{\text{combustion}}$, of oxalic acid, $H_2C_2O_4(s)$, is -246.05 kJ mol^{-1}. Consider the following data:

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$C(s)$	0	5.69
$CO_2(g)$	−393.5	213.6
$H_2(g)$	0	130.6
$H_2O(l)$	−285.8	69.96
$O_2(g)$	0	205.0
$H_2C_2O_4(s)$	?	120.1

(a) Write the balanced thermochemical equation that describes the combustion of one mole of oxalic acid.

(b) Write the balanced thermochemical equation that describes the formation of one mole of oxalic acid.

(c) Use the information in the table above and the equations in parts (a) and (b) to calculate ΔH_f° for oxalic acid.

(d) Calculate ΔS_f° for oxalic acid and ΔS° for the combustion of one mole of oxalic acid.

(e) Calculate ΔG_f° for oxalic acid and ΔG° for the combustion of one mole of oxalic acid.

OH **19.109** Many biochemical reactions have positive values for ΔG° and seemingly should not be expected to be spontaneous. They occur, however, because they are chemically coupled with other reactions that have negative values of ΔG°. An example is the set of reactions that forms the beginning part of the sequence of reactions involved in the metabolism of glucose, a sugar. Given these reactions and their corresponding ΔG° values,

$$\text{glucose} + \text{phosphate} \longrightarrow \text{glucose 6-phosphate} + H_2O \qquad \Delta G° = +13.13 \text{ kJ}$$

$$\text{ATP} + H_2O \longrightarrow \text{ADP} + \text{phosphate} \qquad \Delta G° = -32.22 \text{ kJ}$$

calculate $\Delta G°$ for the coupled reaction

$$\text{glucose} + \text{ATP} \longrightarrow \text{glucose 6-phosphate} + \text{ADP}$$

***19.110** The reaction

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

has $\Delta G° = -5407$ kJ. Determine the value of $\Delta G_f°$ for $C_4H_{10}(g)$. Calculate the value of K_c for the reaction at 25 °C.

***19.111** At 1500 °C, $K_c = 5.67$ for the reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Calculate the value of $\Delta G°_{1773}$ for the reaction at this temperature.

19.112 Given the following reactions and their values of $\Delta G°$, calculate the value of $\Delta G_f°$ for $N_2O_5(g)$.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta G° = -474.4 \text{ kJ}$$

$$N_2O_5(g) + H_2O(l) \longrightarrow 2HNO_3(l) \qquad \Delta G° = -37.6 \text{ kJ}$$

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}H_2(g) \longrightarrow HNO_3(l) \qquad \Delta G° = -79.91 \text{ kJ}$$

***19.113** At room temperature (25 °C), the gas ClNO is impure because it decomposes slightly according to the equation

$$2ClNO(g) \rightleftharpoons Cl_2(g) + 2NO(g)$$

The extent of decomposition is about 5%. What is the approximate value of $\Delta G°_{298}$ for this reaction at this temperature?

***19.114** The reaction

$$N_2O(g) + O_2(g) \rightleftharpoons NO_2(g) + NO(g)$$

has $\Delta H° = -42.9$ kJ and $\Delta S° = -26.1$ J/K. Suppose 0.100 mol of N_2O and 0.100 mol of O_2 are placed in a 2.00 L container at 475 °C and this equilibrium is established. What percentage of the N_2O has reacted? (*Note:* Assume that ΔH and ΔS are relatively insensitive to temperature, so $\Delta H°_{298}$ and $\Delta S°_{298}$ are about the same as $\Delta H°_{773}$ and $\Delta S°_{773}$, respectively.)

19.115 Use the data in Table 19.3 to calculate the bond energy in the nitrogen molecule and the oxygen molecule.

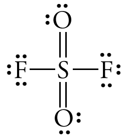
19.116 The heat of vaporization of carbon tetrachloride, CCl_4, is 29.9 kJ mol^{-1}. Using this information and data in Tables 19.3 and 19.4, estimate the standard heat of formation of liquid CCl_4.

19.117 At 25 °C, 0.0560 mol O_2 and 0.020 mol N_2O were placed in a 1.00 L container where the following equilibrium was then established.

$$2N_2O(g) + 3O_2(g) \rightleftharpoons 4NO_2(g)$$

At equilibrium, the NO_2 concentration was 0.020 *M*. Calculate the value of $\Delta G°$ for the reaction.

19.118 For the substance $SO_2F_2(g)$, $\Delta H_f° = -858$ kJ mol^{-1}. The structure of the SO_2F_2 molecule is



Use the value of the S—F bond energy calculated in Problem 19.94 and the data in Appendix C.3 to determine the average S═O bond energy in SO_2F_2 in units of kJ mol^{-1}.

| Multi-Concept Questions

***19.119** Ethyl alcohol, C_2H_5OH, has been suggested as an alternative to gasoline as a fuel. In Example 19.5 we calculated $\Delta G°$ for combustion of 1 mol of C_2H_5OH; in Example 19.6 we calculated $\Delta G°$ for combustion of 1 mol of octane. Let's assume that gasoline has the same properties as octane (one of its constituents). The density of C_2H_5OH is 0.7893 g/mL; the density of octane, C_8H_{18}, is 0.7025 g/mL. Calculate the maximum work that could be obtained by burning 1 gallon (3.78 liters) each of C_2H_5OH and C_8H_{18}. On a *volume* basis, which is the better fuel?

***19.120** When solutions of sodium hydroxide are used to neutralize hydrochloric acid, the standard heat of reaction is found to be −55.86 kJ. When propionic acid $HC_3H_5O_2$ is neutralized with sodium hydroxide the standard heat of the reaction is −49.23 kJ. What is the standard heat and entropy change for the ionization of propionic acid?

***19.121** You've recently inherited a fortune and immediately after that an inventor approaches you with the investment deal of a lifetime. The inventor has found a "system" to react water with methane to make methanol and hydrogen gas, two potentially valuable fuels. In your interview with the inventor, it is claimed that a revolutionary new catalyst shifts the equilibrium position of the reaction to favor products and that 134 kg of methanol are produced for each 117 cubic meters of methane used (at STP). Use your knowledge of chemical principles to find all of the flaws in this project before deciding to risk your new fortune on it.

***19.122** A certain weak acid has a pK_a of 5.83. When 100.0 mL of a 0.00525 *M* solution of this weak acid at 21.26 °C is reacted with 45.6 mL of 0.00634 *M* sodium hydroxide ($HA + OH^- \longrightarrow A^- + H_2O$) at 22.18 °C, the temperature of the mixture rises to 24.88 °C. What is the entropy change associated with the ionization ($HA \longrightarrow A^- + H^+$) of this weak acid? (Assume that the volumes are additive and the densities of the two solutions are 1.000 g cm^{-3}, with a specific heat that is the same as pure water.)

Exercises in Critical Thinking

19.123 On earth, we do not normally find collections of individual subatomic particles, such as protons, neutrons, and electrons. Rather, they are assembled into atoms of various kinds. On the other hand, in the interior of stars individual atoms don't exist. There, an atom would break apart into separate subatomic particles. Explain this in terms of the principles of thermodynamics.

19.124 The average C—H bond energy calculated using the procedure in Section 19.10 is not quite equal to the energy needed to cause the reaction $CH_4(g) \longrightarrow CH_3(g) + H(g)$. Suggest reasons why this is so.

19.125 Discuss this statement: A world near absolute zero would be controlled almost entirely by potential energy. NASA states that the average temperature of the universe is 2.73 K. What does this mean about the universe?

19.126 If a catalyst were able to affect the position of equilibrium in a reaction, it would be possible to construct a perpetual motion machine (a machine from which energy could be extracted without having to put energy into it). Imagine how such a machine could be made. Why would it violate the first law of thermodynamics?

19.127 At the beginning of this chapter we noted that the reaction of CO_2 with H_2O to form a hydrocarbon fuel is nonspontaneous. According to thermodynamics, where would the position of equilibrium lie for such a reaction. Why?

20 Electrochemistry

Chapter Outline

20.1 | Galvanic (Voltaic) Cells

20.2 | Cell Potentials

20.3 | Standard Reduction Potentials

20.4 | E°_{cell} and ΔG°

20.5 | Cell Potentials and Concentrations

20.6 | Electricity

20.7 | Electrolytic Cells

20.8 | Electrolysis Stoichiometry

20.9 | Practical Applications of Electrolysis

Governments around the world are coming to the conclusion that we must develop "green" economic and consumption policies that are sustainable far into the future. This means that the use of resources should be minimized, and those resources that are used for a wide variety of human activities must be replenished rapidly. One way to achieve a sustainable energy economy is to convert solar and wind energy directly into electricity, bypassing petroleum and all of its production, refining, and pollution problems. The smart car shown in this photo can utilize green energy sources with a minimum impact on nonrenewable resources. age fotostock/SuperStock

This Chapter in Context

Oxidation and reduction (redox) reactions occur in many chemical systems. Examples include our own respiratory system and the complementary photosynthetic system in plants. In addition there's the toasting of bread, the rusting of iron, the action of bleach on stains, and the production and combustion of petroleum that heats us, generates electricity, and moves our cars. In this chapter we will study how it is possible to separate the processes of oxidation (electron loss) and reduction (electron gain) and cause them to occur in different physical locations. When we are able to do this, we can use spontaneous redox reactions to produce electricity. And by reversing the process, we can use electricity to make nonspontaneous redox reactions happen to produce important products by a process called *electrolysis.*

Because electricity plays a role in these systems, the processes involved are described as **electrochemical changes**. The study of such changes is called **electrochemistry**. As you will learn, electrical measurements and the principles of thermodynamics combine to give fundamental information about chemical reactions, such as free energy changes and equilibrium constants.

The last section of this chapter describes modern batteries. Solar and wind energy are generally thought to be environmentally benign methods for generating electricity. Development of new, highly efficient, light, and relatively inexpensive batteries and fuel cells is an area of intensive research so that solar and wind power can become important contributors to fuel conservation efforts.

20.1 | Galvanic (Voltaic) Cells

Batteries have become common sources of portable power for a wide range of consumer products, from cell phones to iPods to laptops and hybrid cars. The energy from a battery comes from a spontaneous redox reaction in which the electron transfer is forced to take place through a wire. The apparatus that provides electricity in this way is called a **galvanic cell**, after Luigi Galvani (1737–1798), an Italian anatomist who discovered that electricity can cause the contraction of muscles. (It is also called a **voltaic cell**, after another Italian scientist Allesandro Volta (1745–1827), whose inventions led ultimately to the development of modern batteries.)

Construction of a Galvanic Cell

If a shiny piece of metallic copper is placed into an aqueous solution of silver nitrate, a spontaneous reaction occurs. Gradually, a grayish white deposit forms on the copper and the liquid itself becomes pale blue as hydrated Cu^{2+} ions enter the solution (see Figure 20.1). The equation for this reaction is

$$2Ag^{+}(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

Although the reaction is exothermic, no usable energy can be harnessed from it because all the energy is dispersed as heat.

To produce useful *electrical* energy, the two half-reactions involved in the net reaction must be made to occur in separate containers or compartments called **half-cells.** When this is done, electrons must flow through an external circuit to power devices such as a laser pointer, a laptop computer, or your iPod. An apparatus to accomplish this—a **galvanic**

■ A galvanic cell is composed to two half-cells connected by an external circuit and a salt bridge.

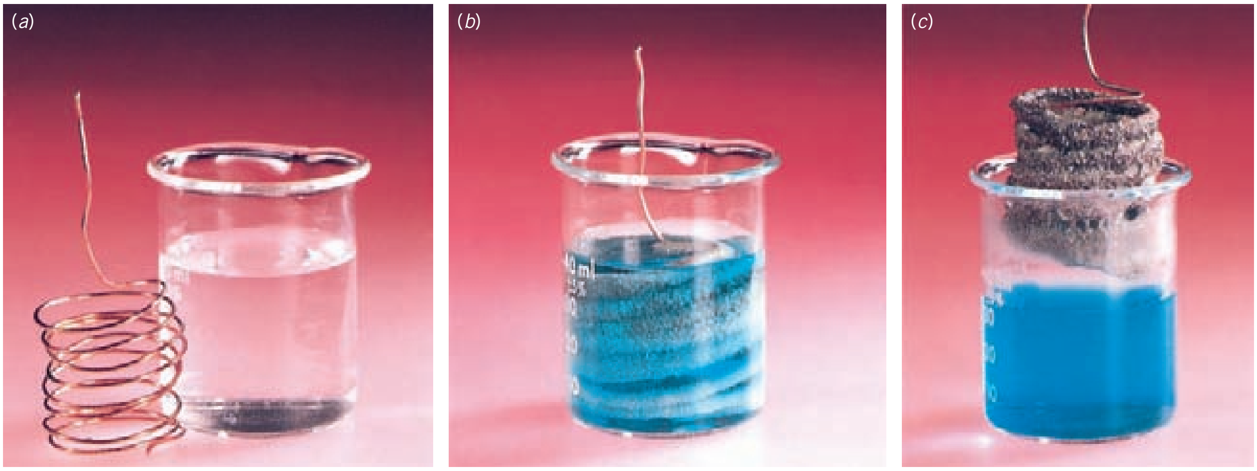


Figure 20.1 | **Reaction of copper with a solution of silver nitrate.** (*a*) A coil of copper wire stands next to a beaker containing a silver nitrate solution. (*b*) When the copper wire is placed in the solution, copper dissolves, giving the solution its blue color, and metallic silver deposits as glittering crystals on the wire. (*c*) After a while, much of the copper has dissolved and nearly all of the silver has deposited as the free metal. *(Michael Watson)*

cell—is made up of two half-cells, as illustrated in Figure 20.2. On the left, a silver electrode dips into a solution of $AgNO_3$, and, on the right, a copper electrode dips into a solution of $Cu(NO_3)_2$. The two electrodes are connected by an external electrical circuit and the two solutions are connected by a *salt bridge*, the function of which will be described shortly. When the circuit is completed by closing the switch, the reduction of Ag^+ to Ag occurs spontaneously in the half-cell on the left and oxidation of Cu to Cu^{2+} occurs spontaneously in the half-cell on the right. The reaction that takes place in each half-cell is a *half-reaction* of the type you learned to balance by the ion-electron method in Chapter 6. In the silver half-cell, the following half-reaction occurs.

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{(reduction)}$$

In the copper half-cell, the half-reaction is

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$

When these reactions take place, electrons left behind by oxidation of the copper travel through the external circuit to the other electrode where they are transferred to the silver ions, as Ag^+ is reduced to the familiar shiny silver metal.

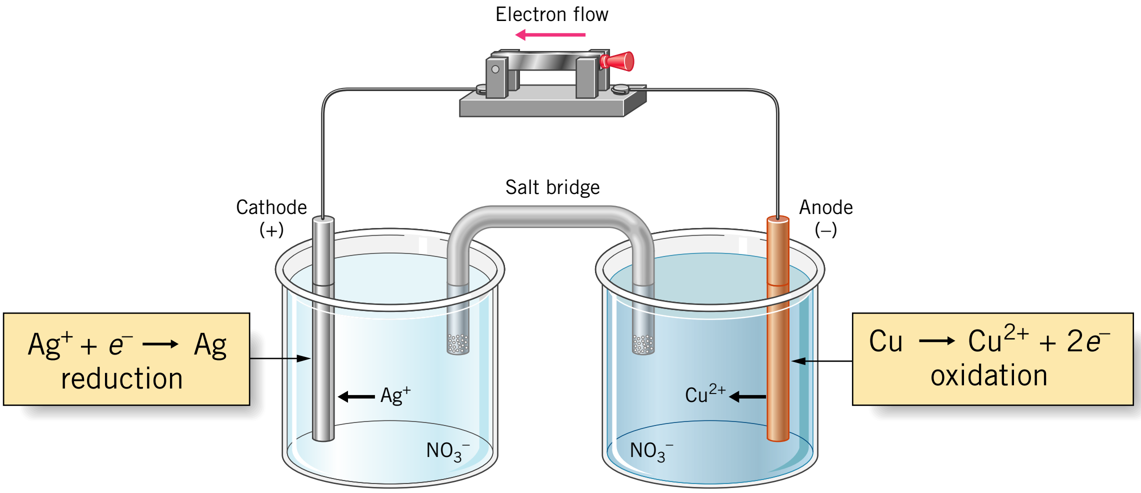


Figure 20.2 | **A galvanic cell.** The cell consists of two half-cells. Oxidation takes place in one half-cell and reduction in the other as indicated by the half-reactions.

Cell Reactions

The overall reaction that takes place in the galvanic cell is called the **cell reaction**. To obtain it, we combine the individual electrode half-reactions, making sure that the number of electrons gained in one half-reaction equals the number lost in the other. Thus, to obtain the cell reaction we multiply the half-reaction for the reduction of silver by 2 and then add the two half-reactions to obtain the net reaction. (Notice that $2e^-$ appears on each side, and so they cancel.) This is exactly the same process we used to balance redox reactions by the ion–electron method described in Section 6.2.

$$
\begin{array}{rcll}
2\mathrm{Ag}^+(aq) + 2e^- & \longrightarrow & 2\mathrm{Ag}(s) & \text{(reduction)} \\
\mathrm{Cu}(s) & \longrightarrow & \mathrm{Cu}^{2+}(aq) + 2e^- & \text{(oxidation)} \\
\hline
2\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) + \cancel{2e^-} & \longrightarrow & 2\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) + \cancel{2e^-} & \text{(cell reaction)}
\end{array}
$$

■ When electrons appear as a reactant, the process is reduction; when they appear as a product, it is oxidation.

■ The two electrons canceled in this reaction are also the number of electrons transferred. These will be important later when we discuss the Nernst equation.

Naming Electrodes in a Galvanic Cell

The electrodes in electrochemical systems are identified by the names *cathode* and *anode*. The names are *always* assigned according to the nature of the chemical changes that occur at the electrodes. In *all electrochemical systems:*

> The **cathode** is the electrode at which reduction (electron gain) occurs.
>
> The **anode** is the electrode at which oxidation (electron loss) occurs.

TOOLS

Electrode names and reactions

Thus, in the galvanic cell we've been discussing, the silver electrode is the cathode and the copper electrode is the anode.

Conduction of Charge

In the external circuit of a galvanic cell, electrical charge is transported from one electrode to the other by the movement of *electrons* through the wires. This is called **metallic conduction,** and it is how metals in general conduct electricity. In this external circuit, electrons always travel from the anode, where they are a product of the oxidation process, to the cathode, where they are picked up by the substance being reduced.

In electrochemical cells another kind of electrical conduction also takes place. In a solution that contains ions (or in a molten ionic compound), *electrical charge is carried through the liquid by the movement of ions, not electrons.* The transport of electrical charge by ions is called **electrolytic conduction.**

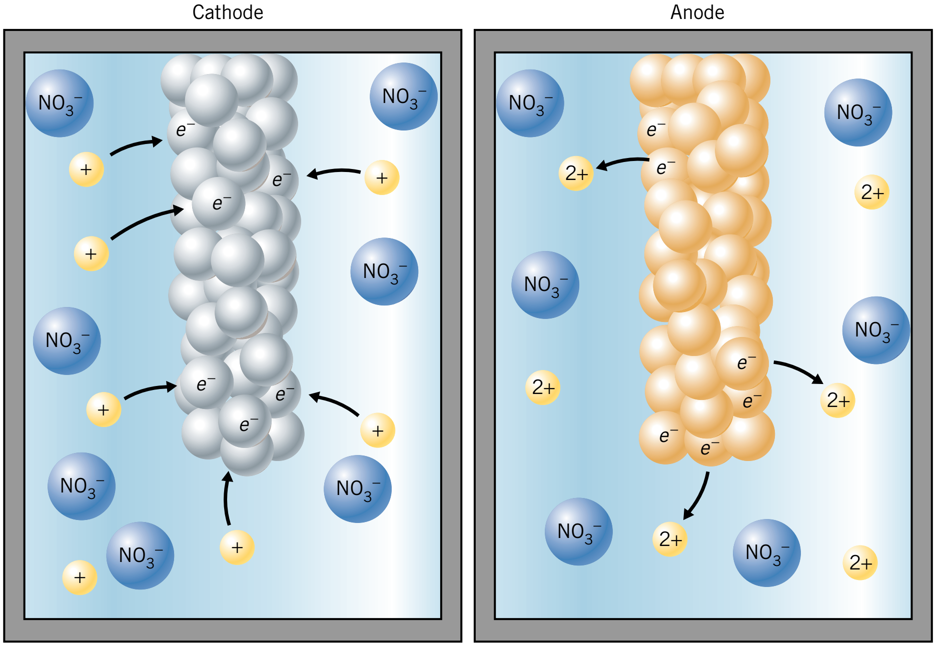
When the reactions take place in the copper–silver galvanic cell, positive copper ions *enter* the liquid that surrounds the anode while positive silver ions *leave* the liquid that surrounds the cathode (Figure 20.3). For the galvanic cell to work, the solutions in both half-cells must remain electrically neutral. This requires that ions be permitted to enter or leave the solutions. For example, when copper is oxidized, the solution surrounding the anode becomes filled with Cu^{2+} ions, so negative ions are needed to balance their charge. Similarly, when Ag^+ ions are reduced, $\mathrm{NO_3}^-$ ions are left behind in the solution and positive ions are needed to maintain neutrality. The **salt bridge** shown in Figure 20.2 allows the movement of ions required to keep the solutions electrically neutral. The salt bridge is also essential to complete the electrical circuit.

A salt bridge is a tube filled with a solution of a salt composed of ions not involved in the cell reaction. Often $\mathrm{KNO_3}$ or KCl is used. The tube is fitted with porous plugs at each end that prevent the solution from pouring out, but at the same time enabling the solution in the salt bridge to exchange ions with the solutions in the half-cells.

During operation of the cell, negative ions can diffuse from the salt bridge into the copper half-cell, or, to a much smaller extent, Cu^{2+} ions can leave the solution and enter the salt bridge. Both processes help keep the copper half-cell electrically neutral. In the silver half-cell, positive ions from the salt bridge can enter or negative $\mathrm{NO_3}^-$ ions can, once again to a much smaller extent, leave the half-cell by entering the salt bridge, to keep it electrically neutral, too.

■ Often the salt bridge is prepared by saturating a hot agar–agar solution with $\mathrm{KNO_3}$ or KCl. After pouring into a U-shaped tube the agar–agar solidifies on cooling. The salt ions can move but the agar–agar does not flow out of the salt bridge.

Figure 20.3 | **Expanded view of Figure 20.2 to show changes that take place at the anode and cathode in the copper–silver galvanic cell.** (Not drawn to scale.) At the anode, Cu^{2+} ions enter the solution when copper atoms are oxidized, leaving electrons behind on the electrode. Unless Cu^{2+} ions move away from the electrode or NO_3^- ions move toward it, the solution around the electrode will become positively charged. At the cathode, Ag^+ ions leave the solution and become silver atoms by acquiring electrons from the electrode surface. Unless more silver ions move toward the cathode or negative ions move away, the solution around the electrode will become negatively charged.



Reduction of silver ions at the cathode extracts electrons from the electrode, so the electrode becomes positively charged.

Oxidation of copper atoms at the anode leaves electrons behind on the electrode, which becomes negatively charged.

Without the salt bridge, electrical neutrality could not be maintained and no electrical current could be produced by the cell. Therefore, *electrolytic contact*—contact by means of a solution containing ions—must be maintained for the cell to function.

If we look closely at the overall movement of ions during the operation of the galvanic cell, we find that negative ions (*anions*) move away from the cathode, where they are present in excess, and *toward the anode*, where they are needed to balance the charge of the positive ions being formed. Similarly, we find that positive ions (*cations*) move away from the anode, where they are in excess, and *toward the cathode*, where they can balance the charge of the anions left in excess. In fact, the reason positive ions are called cations and negative ions are called anions is because of the nature of the electrodes toward which they move. In summary:

> Cations move in the general direction of the cathode.
>
> Anions move in the general direction of the anode.

Charges of the Electrodes

■ The small difference in charge between the electrodes is formed by the spontaneity of the overall reaction, that is, by the favorable free energy change. Nature's tendency toward electrical neutrality prevents a large buildup of charge on the electrodes and promotes the spontaneous flow of electricity through the external circuit.

At the anode of the galvanic cell described in Figures 20.2 and 20.3, copper atoms spontaneously leave the electrode and enter the solution as Cu^{2+} ions. The electrons that are left behind give the anode a slight negative charge. (We say the anode has a *negative polarity*.) At the cathode, electrons spontaneously join Ag^+ ions to produce neutral atoms, but the effect is the same as if Ag^+ ions become part of the electrode, so the cathode acquires a slight positive charge. (The cathode has a *positive polarity*.) During the operation of the cell, the amount of positive and negative charge on the electrodes is kept small by the flow of electrons (an electric current) through the external circuit from the anode to the cathode when the circuit is complete. In fact, unless electrons can flow out of the anode and into the cathode, the chemical reactions that occur at their surfaces will cease.

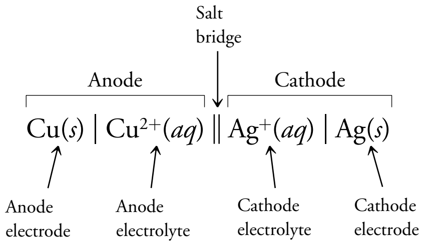
Standard Cell Notation

As a matter of convenience, chemists have devised a shorthand way of describing the makeup of a galvanic cell. For example, the copper–silver cell that we have been using in our discussion is represented as follows:

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

By convention, in **standard cell notation**, the anode half-cell is specified on the left, with the electrode material of the anode given first. In this case, the anode is copper metal. The single vertical bar represents the *phase boundary* between the copper electrode and the solution that surrounds it. The double vertical bars represent the two phase boundaries, one at each end of the salt bridge, which connects the solutions in the two half-cells. On the right, the cathode half-cell is described, with the material of the cathode given last. Thus, the electrodes themselves (copper and silver) are specified at opposite ends of the cell description.

■ Standard cell notation is also called a cell diagram.



■ In the anode compartment, Cu is the reactant and is oxidized to Cu^{2+}, whereas in the cathode compartment, Ag^+ is the reactant and is reduced to Ag.

Sometimes, both the oxidized and reduced forms of the reactants in a half-cell are soluble and cannot be used as an electrode. In these cases, an inert electrode composed of platinum or gold is used to provide a site for electron transfer. For example, a galvanic cell can be made using an anode composed of a zinc electrode dipping into a solution containing Zn^{2+} and a cathode composed of a platinum electrode dipping into a solution containing both Fe^{2+} and Fe^{3+} ions. The cell reaction is

$$2Fe^{3+}(aq) + Zn(s) \longrightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

The cell notation for this galvanic cell is written as follows:

$$Zn(s) \mid Zn^{2+}(aq) \parallel Fe^{2+}(aq), Fe^{3+}(aq) \mid Pt(s)$$

where we have separated the formulas for the two iron ions by a comma. In this cell, the reduction of the Fe^{3+} to Fe^{2+} takes place at the surface of the inert platinum electrode.

■ Since they are thoroughly mixed in solution, it does not matter if Fe^{2+} or Fe^{3+} is written first.

Example 20.1
Describing Galvanic Cells

The following spontaneous reaction occurs when metallic zinc is dipped into a solution of copper sulfate.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

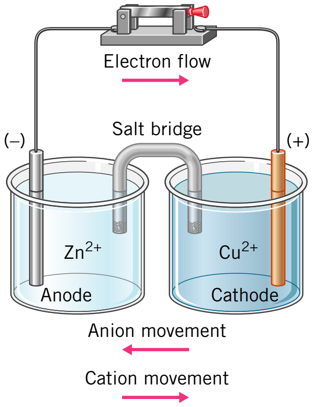
Describe a galvanic cell that could take advantage of this reaction. What are the half-cell reactions? What is the standard cell notation? Make a sketch of the cell and label the cathode and anode, the charges on each electrode, the direction of ion flow, and the direction of electron flow.

■ **Analysis:** Answering all these questions relies on identifying the anode and cathode in the equation for the cell reaction; this is often the key to solving problems of this type. By definition, the anode is the electrode at which oxidation happens, and the cathode is where reduction occurs.

■ **Assembling the Tools:** We can use the principles of the ion–electron method for balancing redox reactions that were learned in Section 6.2. When the half-reactions are balanced, the one with electrons as reactants is the reduction half-reaction and the one where electrons are products is the oxidation half-reaction.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(anode reaction)}$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad \text{(cathode reaction)}$$

We will use the procedures just discussed to write the standard cell notation and draw our diagram.



The zinc-copper cell. In the cell notation described in this example, we indicate the anode on the left and the cathode on the right. In this drawing of the apparatus, the anode half-cell is also shown on the left, but it could just as easily be shown on the right, as in Figure 20.2. Be sure you understand that where we place the apparatus on the lab bench doesn't affect which half-cell is the anode and which is the cathode.

■ **Solution:** We start writing the standard cell notation with the anode itself. Since Zn(*s*) is a metal, it can be used as the anode. The anode half-cell is therefore a zinc electrode dipping into a solution that contains Zn^{2+} [e.g., from dissolved $Zn(NO_3)_2$ or $ZnSO_4$]. Symbolically, the anode half-cell is written with the electrode material at the left of the vertical bar and the oxidation product at the right.

$$Zn(s) \mid Zn^{2+}(aq)$$

Copper ions gain electrons and are reduced to metallic copper, which we can use as the cathode. So the cathode half-cell consists of a copper electrode dipping into a solution containing Cu^{2+} [e.g., from dissolved $Cu(NO_3)_2$ or $CuSO_4$]. The copper half-cell is represented with the electrode material to the right of the vertical bar and the substance reduced on the left.

$$Cu^{2+}(aq) \mid Cu(s)$$

The standard cell notation places the zinc anode half-cell on the left and the copper cathode half-cell on the right, separated by double bars that represent the salt bridge.

$$\underbrace{Zn(s) \mid Zn^{2+}(aq)}_{\text{anode}} \parallel \underbrace{Cu^{2+}(aq) \mid Cu(s)}_{\text{cathode}}$$

A sketch of the cell is shown in the margin. The anode always carries a negative charge in a galvanic cell, so the zinc electrode is negative and the copper electrode is positive. Electrons in the external circuit travel from the negative electrode to the positive electrode (i.e., from the Zn anode to the Cu cathode). Anions move toward the anode and cations move toward the cathode. In the salt bridge we also find that anions will flow toward the anode and cations toward the cathode as shown.

■ **Are the Answers Reasonable?** All of the answers depend on determining which substance is oxidized and which is reduced, so we check that first. Oxidation is electron loss, and Zn must lose electrons to become Zn^{2+}, so zinc is oxidized and must be the anode. If zinc is the anode, then copper must be the cathode. We can then reason that the oxidation of zinc produces electrons that flow from the anode to the cathode.

Practice Exercises

20.1 | Sketch and label a galvanic cell that makes use of the following spontaneous redox reaction.

$$Mg(s) + Fe^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Fe(s)$$

Write the half-reactions for the anode and cathode. Give the standard cell notation. (*Hint*: Determine which half-reaction represents oxidation and which represents reduction.)

20.2 | Write the anode and cathode half-reactions for the following galvanic cell. Write the equation for the overall cell reaction.

$$Al(s) \mid Al^{3+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$$

Sketch and label a galvanic cell that corresponds to this standard cell notation.

20.2 | Cell Potentials

■ The potential generated by a galvanic cell has also been called the **electromotive force (emf)**. Modern electrochemistry uses the preferred E_{cell} or E°_{cell} to note cell potentials and standard cell potentials, respectively.

A galvanic cell has an ability to push electrons through the external circuit. The magnitude of this ability is expressed as a **potential**. Potential is expressed in an electrical unit called the **volt (V)**, which is a measure of the amount of energy, in joules, that can be delivered per **coulomb** (the SI unit of charge) as the charges move through the circuit. Thus, a charge flowing under a potential of 1 volt can deliver 1 joule of energy per coulomb.

$$1 \text{ V} = 1 \text{ J/C} \tag{20.1}$$

The voltage or potential of a galvanic cell varies with the amount of charge flowing through the circuit. The *maximum* potential that a given cell can generate is called its **cell potential, E_{cell},** and it depends on the composition of the electrodes, the concentrations of the ions in the half-cells, and the temperature. The standard state for electrochemistry is defined as a system where the temperature is 25 °C, all concentrations are 1.00 *M*, and any gases are at 1.00 atm pressure. When the system is at standard state, the potential of a galvanic cell is the **standard cell potential,** symbolized by E°_{cell}.

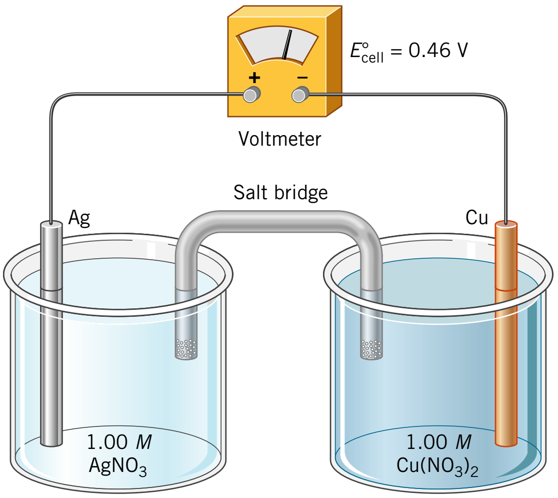


Figure 20.4 | **A cell designed to generate the standard cell potential.** The concentrations of the Cu^{2+} and Ag^+ ions in the half-cells are 1.00 *M*. It is very important to always connect the negative terminal of the voltmeter to the anode for correct readings.

Cell potentials are rarely larger than a few volts. For example, the standard cell potential for the galvanic cell constructed from silver and copper electrodes shown in Figure 20.4 is only 0.46 V, and one cell in an automobile battery produces only about 2 V. Batteries that generate higher voltages, such as the automobile battery, contain a number of cells connected one after the other (i.e., in series) so that their potentials are additive.

In Section 20.5 we will see that we can calculate the cell potential, E_{cell}, for systems that are not at standard state. As long as we know the temperature, concentration of solutes and pressures of gases, we will be able to calculate how much the cell potential differs from the standard cell potential. Without getting into the details that are presented later, it is important to note that in most cases the standard cell potential and the calculated cell potential for a reaction usually differ by less than 0.5 volt and usually have the same algebraic sign. Therefore we will make generalizations and demonstrate them using standard reduction potentials. These generalizations will usually apply to nonstandard state cell potentials.

■ If charge flows from a cell, some of the cell's voltage is lost overcoming its own internal resistance, and the measured voltage is less than the original E_{cell}.

Reduction Potentials

It is useful to think of each half-cell as having a certain natural tendency to acquire electrons and proceed as a *reduction*. The magnitude of this tendency is expressed by the half-reaction's **reduction potential.** When measured under standard conditions, namely, 25 °C, concentrations of 1.00 *M* for all solutes, and pressures of 1 atm for all gases, the reduction potential is called the **standard reduction potential.** To represent a standard reduction potential, we will add a subscript to the symbol $E°$ that identifies the substance undergoing reduction. Thus, the standard reduction potential for the half-reaction

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

is specified as $E^\circ_{Cu^{2+}}$.

■ Standard reduction potentials are also called **standard electrode potentials**.

When two half-cells are connected to make a Galvanic cell, the one with the larger standard reduction potential (the one with the greater tendency to undergo reduction) acquires electrons from the half-cell with the lower standard reduction potential, which is therefore forced to undergo oxidation. The standard cell potential, which is always taken to be a positive number, represents the *difference* between the standard reduction potential of one half-cell and the standard reduction potential of the other. In general, therefore,

$$E^\circ_{cell} = \begin{pmatrix}\text{standard reduction}\\ \text{potential of the}\\ \text{substance reduced}\end{pmatrix} - \begin{pmatrix}\text{standard reduction}\\ \text{potential of the}\\ \text{substance oxidized}\end{pmatrix} \tag{20.2}$$

■ In a galvanic cell, the measured cell potential is *always* taken to be a positive value. This is important to remember.

TOOLS

Standard reduction potentials used to calculate E°_{cell}

As an example, let's look at the copper–silver cell. From the cell reaction,

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$

we can see that silver ions are reduced and copper is oxidized. If we compare the two possible reduction half-reactions,

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

the one for Ag^+ must have a greater tendency to proceed than the one for Cu^{2+}, because it is the silver ion that is actually reduced. This means that the standard reduction potential of Ag^+ must be more positive than the standard reduction potential of Cu^{2+}. In other words, if we knew the values of $E^\circ_{Ag^+}$ and $E^\circ_{Cu^{2+}}$, we could calculate E°_{cell} with Equation 20.2 by subtracting the less positive standard reduction potential (copper) from the more positive one (silver), always resulting in a positive number.

■ Notice that we use the standard cell potentials without any adjustment for the number of electrons in the half reaction.

$$E^\circ_{cell} = E^\circ_{Ag^+} - E^\circ_{Cu^{2+}}$$

The Hydrogen Electrode

Unfortunately there is no way to measure the standard reduction potential of an isolated half-cell. All we can measure is the difference in potential produced when two half-cells are connected. Therefore, to assign numerical values for standard reduction potentials, a reference electrode has been arbitrarily chosen and its standard reduction potential has been defined as *exactly* ***zero volts.*** This reference electrode is called the **standard hydrogen electrode** (see Figure 20.5). Gaseous hydrogen at a pressure of 1.00 atm is bubbled over a platinum electrode coated with very finely divided platinum, which provides a large catalytic surface area on which the electrode reaction can occur. This electrode is surrounded by a solution whose temperature is 25 °C and in which the hydrogen ion concentration is 1.00 *M*. The half-cell reaction at the platinum surface, written as a reduction, is

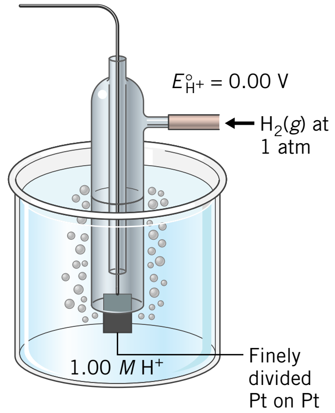


Figure 20.5 | **The hydrogen electrode.** The half-reaction is $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$.

$$2H^+(aq,\ 1.00\ M) + 2e^- \rightleftharpoons H_2(g,\ 1.00\ \text{atm}) \qquad E^\circ_{H^+} \equiv 0\ \text{V (exactly)}$$

The double arrows indicate only that the reaction is reversible, not that there is true equilibrium. Whether the half-reaction occurs as reduction or oxidation depends on the standard reduction potential of the half-cell with which it is paired.

Figure 20.6 illustrates the hydrogen electrode connected to a copper half-cell to form a galvanic cell. When we use a voltmeter to measure the potential of the cell, we find that the copper electrode has a positive charge and the hydrogen electrode has a negative charge. Therefore, copper must be the cathode, and Cu^{2+} is reduced to Cu when the cell operates. Similarly, hydrogen must be the anode, and H_2 is oxidized to H^+. The half-reactions and cell reaction, therefore, are

$$\begin{array}{rcll} Cu^{2+}(aq) + 2e^- & \longrightarrow & Cu(s) & \text{(cathode)} \\ H_2(g) & \longrightarrow & 2H^+(aq) + 2e^- & \text{(anode)} \\ \hline Cu^{2+}(aq) + H_2(g) & \longrightarrow & Cu(s) + 2H^+(aq) & \text{(cell reaction)}^1 \end{array}$$

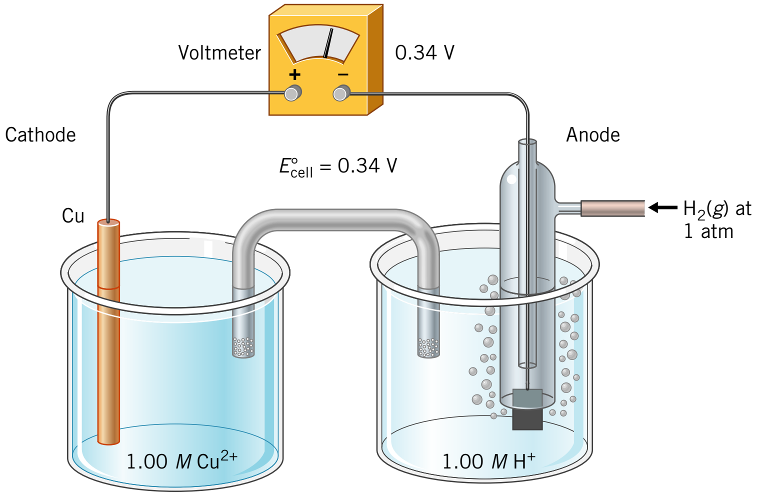


Figure 20.6 | **A galvanic cell composed of copper and hydrogen half-cells.** The cell reaction is $Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$.

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[1] The cell notation for this cell is written as

$$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

The notation for the hydrogen electrode (the anode in this case) is shown at the left of the double vertical bars.

Using Equation 20.2, we can express E°_{cell} in terms of $E^\circ_{\text{Cu}^{2+}}$ and $E^\circ_{\text{H}^+}$.

$$E^\circ_{\text{cell}} = \underset{\substack{\uparrow\\ \text{Reduction potential}\\ \text{of the substance}\\ \text{reduced}}}{E^\circ_{\text{Cu}^{2+}}} - \underset{\substack{\uparrow\\ \text{Reduction potential}\\ \text{of the substance}\\ \text{oxidized}}}{E^\circ_{\text{H}^+}}$$

The measured standard cell potential is 0.34 V, and $E^\circ_{\text{H}^+}$ equals 0.00 V. Therefore,

$$0.34\text{ V} = E^\circ_{\text{Cu}^{2+}} - 0.00\text{ V}$$

Relative to the hydrogen electrode, then, the standard reduction potential of Cu^{2+} is $+0.34$ V. (We have written the value with a plus sign because some standard reduction potentials are negative, as we will see.)

Now let's look at a galvanic cell set up between a zinc electrode and a hydrogen electrode (see Figure 20.7). This time we find that the hydrogen electrode is positive and the zinc electrode is negative, which tells us that the hydrogen electrode is the cathode and the zinc electrode is the anode. This means that the hydrogen ion is being reduced and zinc is being oxidized. Based on this reasoning the half-reactions and cell reaction are

$$\begin{array}{rcll} 2\text{H}^+(aq) + 2e^- & \longrightarrow & \text{H}_2(g) & \text{(cathode)} \\ \text{Zn}(s) & \longrightarrow & \text{Zn}^{2+}(aq) + 2e^- & \text{(anode)} \\ \hline 2\text{H}^+(aq) + \text{Zn}(s) & \longrightarrow & \text{H}_2(g) + \text{Zn}^{2+}(aq) & \text{(cell reaction)}^2 \end{array}$$

From Equation 20.2, the standard cell potential is given by

$$E^\circ_{\text{cell}} = E^\circ_{\text{H}^+} - E^\circ_{\text{Zn}^{2+}}$$

Substituting into this the measured standard cell potential of 0.76 V and $E^\circ_{\text{H}^+} = 0.00$ V, we have

$$0.76\text{ V} = 0.00\text{ V} - E^\circ_{\text{Zn}^{2+}}$$

which gives

$$E^\circ_{\text{Zn}^{2+}} = -0.76\text{ V}$$

Notice that the standard reduction potential of zinc is negative. A negative standard reduction potential simply means that the substance is not as easily reduced as H^+. In this case, it tells us that Zn is oxidized when it is paired with the hydrogen electrode.

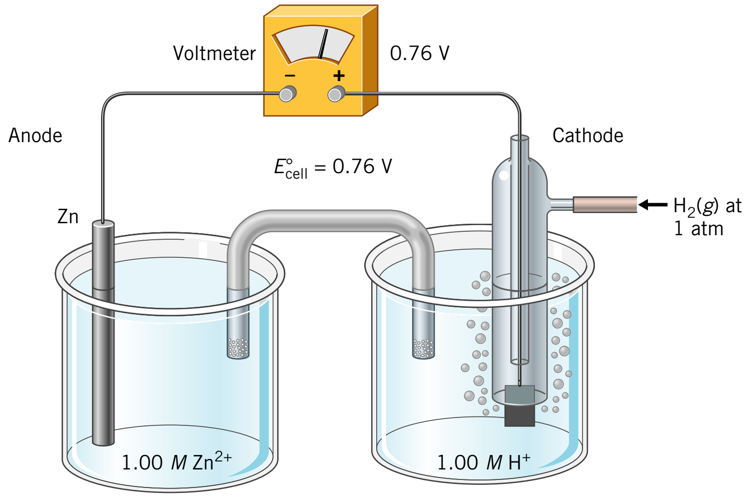


Figure 20.7 | **A galvanic cell composed of zinc and hydrogen half-cells.** The cell reaction is $\text{Zn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$.

---

[2] This cell is represented as

$$\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel \text{H}^+(aq) \mid \text{H}_2(g) \mid \text{Pt}(s)$$

This time the hydrogen electrode is the cathode and appears at the right of the double vertical bars.

The standard reduction potentials of many half-reactions can be compared to that for the standard hydrogen electrode in the manner we just described. Table 20.1 lists values obtained for some typical half-reactions. They are arranged in decreasing order—the half-reactions at the top have the greatest tendency to occur as reductions, while those at the bottom have the least tendency to occur as reduction reactions.

■ Substances located to the left of the double arrows are *oxidizing agents*, because they become reduced when the reactions proceed in the forward direction. The best oxidizing agents are those most easily reduced, and they are located at the top of the table (e.g., F_2).

Table 20.1 Standard Reduction Potentials at 25 °C[a]

Half-Reaction	$E°$ (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$	+1.69
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+1.46
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+1.44
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$	+0.17
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

[a] See Appendix Table C.9 for a more complete listing.

■ Substances located to the right of the double arrows are *reducing agents*; they become oxidized when the reactions proceed from right to left. The best reducing agents are those found at the bottom of the table (e.g., Li).

CHEMISTRY OUTSIDE THE CLASSROOM **20.1**

Corrosion of Iron and Cathodic Protection

A problem that has plagued humanity ever since the discovery of methods for obtaining iron and other metals from their ores has been corrosion—the reaction of a metal with substances in the environment. The rusting of iron in particular is a serious problem because iron and steel have so many uses.

The rusting of iron is a complex chemical reaction that involves both oxygen and moisture (see Figure 1). Iron won't rust in pure water that's oxygen free, and it won't rust in pure oxygen in the absence of moisture. The corrosion process is apparently electrochemical in nature, as shown in the accompanying diagram. At one place on the surface, iron becomes oxidized in the presence of water and enters solution as Fe^{2+}.

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$$

At this location the iron is acting as an anode.

The electrons that are released when the iron is oxidized travel through the metal to some other place where the iron is exposed to oxygen. This is where reduction takes place (it's a cathodic region on the metal surface), and oxygen is reduced to give hydroxide ion.

$$\tfrac{1}{2}O_2(aq) + H_2O + 2e^- \longrightarrow 2OH^-(aq)$$

The iron(II) ions that are formed at the anodic regions gradually diffuse through the water and eventually contact the hydroxide ions. This causes a precipitate of $Fe(OH)_2$ to form, which is very easily oxidized by O_2 to give $Fe(OH)_3$. This hydroxide readily loses water. In fact, complete dehydration gives the oxide,

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$$

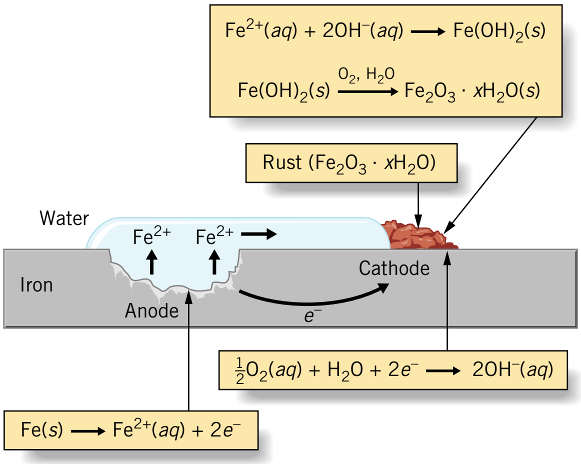
When partial dehydration of the $Fe(OH)_3$ occurs, *rust* is formed. It has a composition that lies between that of the hydroxide and that of the oxide, Fe_2O_3, and is usually referred to as a *hydrated oxide*. Its formula is generally represented as $Fe_2O_3 \cdot xH_2O$.

This mechanism for the rusting of iron explains one of the more interesting aspects of this damaging process. Perhaps you've noticed that when rusting occurs on the body of a car, the rust appears at and around a break (or a scratch) in the surface of the paint, but the damage extends under the painted surface for some distance. Apparently, the Fe^{2+} ions that are formed at the anode sites are able to diffuse rather long distances to the hole in the paint, where they finally react with air to form the rust.

Cathodic Protection

One way to prevent the rusting of iron is to coat it with another metal. This is done with "tin" cans, which are actually steel cans that have been coated with a thin layer of tin. However, if the layer of tin is scratched and the iron beneath is exposed, the corrosion is accelerated because iron has a lower reduction potential than tin; the iron becomes the anode in an electrochemical cell and is easily oxidized.

Another way to prevent corrosion is called *cathodic protection*. It involves placing the iron in contact with a metal that is *more easily* oxidized. This causes iron to be a cathode and the other metal to be the anode. If corrosion occurs, the iron is protected from oxidation because it is cathodic and the other metal reacts instead.



$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$
$Fe(OH)_2(s) \xrightarrow{O_2,\ H_2O} Fe_2O_3 \cdot xH_2O(s)$
Rust ($Fe_2O_3 \cdot xH_2O$)
Water
Fe^{2+}
Fe^{2+}
Iron
Cathode
Anode
e^-
$\tfrac{1}{2}O_2(aq) + H_2O + 2e^- \longrightarrow 2OH^-(aq)$
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Figure 1 **Corrosion of iron.** Iron dissolves in anodic regions to give Fe^{2+}. Electrons travel through the metal to cathodic sites where oxygen is reduced, forming OH^-. The combination of the Fe^{2+} and OH^-, followed by air oxidation, gives rust.

Zinc is most often used to provide cathodic protection to other metals. For example, zinc sacrificial anodes can be attached to the rudder of a boat (see Figure 2). When the rudder is submerged, the zinc will gradually corrode but the metal of the rudder will not. Periodically, the anodes are replaced to provide continued protection.

Steel objects that must withstand the weather are often coated with a layer of zinc, a process called galvanizing. You've probably seen this on chain-link fences and metal garbage pails. Even if the steel is exposed through a scratch, it is not oxidized because it is in contact with a metal that is more easily oxidized.

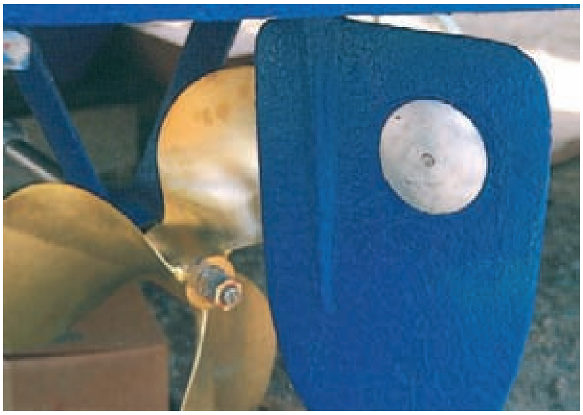


Figure 2 **Cathodic protection.** Before launching, a shiny new zinc anode disk is attached to the bronze rudder of this boat to provide cathodic protection. Over time, the zinc will corrode instead of the less reactive bronze. (The rudder is painted with a special blue paint to inhibit the growth of barnacles.) *(Courtesy James Brady)*

Example 20.2
Calculating Standard Cell Potentials

We mentioned earlier that the standard cell potential of the silver–copper galvanic cell has a value of +0.46 V. The cell reaction is

$$2\text{Ag}^+(aq) + \text{Cu}(s) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)$$

and we have seen that the standard reduction potential of Cu^{2+}, $E^\circ_{\text{Cu}^{2+}}$, is +0.34 V. What is the value of the standard reduction potential of Ag^+, $E^\circ_{\text{Ag}^+}$?

■ Analysis: The standard cell potential is the difference between two standard reduction potentials. Since we know two of these three variables, we just have to be sure our math is correct.

■ Assembling the Tools: We know the standard potential of the cell and one of the two standard reduction potentials, so Equation 20.2 will be our tool to calculate the unknown standard reduction potential. The principles of oxidation and reduction will be used to determine which reactant is reduced and which is oxidized, allowing us to set up the equation correctly.

■ Solution: Silver changes from Ag^+ to Ag; its oxidation number decreases from +1 to 0, so we conclude that Ag^+ is reduced. Similar reasoning tells us that copper is oxidized from Cu to Cu^{2+}. Therefore, according to Equation 20.2,

$$E^\circ_{\text{cell}} = \underbrace{E^\circ_{\text{Ag}^+}}_{\text{Standard reduction potential of substance reduced}} - \underbrace{E^\circ_{\text{Cu}^{2+}}}_{\text{Standard reduction potential of substance oxidized}}$$

Substituting values for E°_{cell} and $E^\circ_{\text{Cu}^{2+}}$,

$$0.46\text{ V} = E^\circ_{\text{Ag}^+} - 0.34\text{ V}$$

Then we solve for $E^\circ_{\text{Ag}^+}$.

$$\begin{aligned} E^\circ_{\text{Ag}^+} &= 0.46\text{ V} + 0.34\text{ V} \\ &= 0.80\text{ V} \end{aligned}$$

The standard reduction potential of silver ion is therefore +0.80 V.

■ Is the Answer Reasonable? We know the standard cell potential is the difference between the two standard reduction potentials. The difference between +0.80 V and +0.34 V (subtracting the smaller from the larger) is 0.46 V. Our calculated standard reduction potential for Ag^+ appears to be correct. You can also take a peek at Table 20.1 now for a final check.

Practice Exercises

20.3 | Copper metal and zinc metal will both reduce Ag^+ ions under standard state conditions. Which metal when used as an electrode in a galvanic cell will have the larger E°_{cell} under these conditions? (*Hint*: Write the two possible chemical reactions.)

20.4 | The galvanic cell described in Practice Exercise 20.1 has a standard cell potential of 1.93 V. The standard reduction potential of Mg^{2+} corresponding to the half-reaction $\text{Mg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mg}(s)$ is −2.37 V. Calculate the standard reduction potential of iron(II). Check your answer by referring to Table 20.1.

At this point you may have wondered why the term *cell potential* is used in some places and *standard cell potential* is used in others. Based on our definitions, the term standard cell potential is used in places where the system is at standard state (i.e., 1.00 *M* concentrations, 1.00 *atm* pressures, and 25.0 °C). Cell potential is used for *any* set of concentrations, pressures, and temperatures, including the standard conditions. For convenience, our calculations in the next two sections will use standard cell potentials.

20.3 | Standard Reduction Potentials

In the previous section we saw how to define standard reduction potentials and standard cell potentials. In addition, by defining the standard reduction potential of the hydrogen electrode, we saw that standard reduction potentials could be determined. Now we will begin investigating some of the uses of standard cell potentials.

Predicting Spontaneous Reactions

It's easy to predict the spontaneous reaction when the substances in two half-reactions, at standard state, are mixed together. This is because we know that *the half-reaction with the more positive reduction potential always takes place as written (namely, as a reduction), while the other half-reaction is forced to run in reverse (as an oxidation).*

■ Strictly speaking, the $E°$ values only tell us what to expect under standard conditions. However, only when $E°_{\text{cell}}$ is small can changes in the concentrations change the direction of the spontaneous reaction.

Example 20.3

Predicting a Spontaneous Reaction

What spontaneous reaction occurs if Cl_2 and Br_2 are added to a solution that contains both Cl^- and Br^-? Assume standard conditions.

■ **Analysis:** We know that in the spontaneous redox reaction, the more easily reduced substance will be the one that undergoes reduction. We need the data to decide which substance will be reduced, Cl_2 or Br_2; we already know that neither Cl^- nor Br^- can be reduced since they cannot be in lower oxidation states.

■ **Assembling the Tools:** By assuming we are at standard state, we can use the standard reduction potentials for Cl_2 and Br_2 in Table 20.1 to compare their $E°$ values to determine the combination that results in a spontaneous reaction. There are two possible reduction half-reactions:

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$$
$$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$$

and we need to decide which is the reduction and which is the oxidation half-reaction. This is the spontaneous reaction, so Equation 20.2 must yield a positive result *whether or not the reaction occurs in a galvanic cell.*

■ **Solution:** Referring to Table 20.1, we find that Cl_2 has a more positive standard reduction potential (+1.36 V) than does Br_2 (+1.07 V). This means Cl_2 will be reduced and the half-reaction for Br_2 will be reversed, changing it to an oxidation process. Therefore, the spontaneous reaction has the following half-reactions.

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq) \qquad \text{(a reduction)}$$
$$2Br^-(aq) \longrightarrow Br_2(aq) + 2e^- \qquad \text{(an oxidation)}$$

The net reaction is obtained by combining the half-reactions.

$$Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$$

■ **Is the Answer Reasonable?** We can check to be sure we've read the correct values for $E°_{Cl_2}$ and $E°_{Br_2}$ from Table 20.1, and we can check the half-reactions we used to find the equation for the net reaction. (Experimentally, chlorine does indeed oxidize bromide ion to bromine, a fact used to recover bromine from seawater and natural brine solutions.)

When conditions are at standard state, reactants and products of *spontaneous* redox reactions are easy to spot when standard reduction potentials are listed in order of most positive to least positive (most negative), as in Table 20.1. For *any* pair of half-reactions, the one higher up in the table has the more positive standard reduction potential and occurs as a reduction. The other half-reaction is reversed and occurs as an oxidation. *Therefore, for a spontaneous reaction, the* ***reactants*** *are found on the left side of the higher half-reaction and on the right side of the lower half-reaction. (Also, this is usually, but not always, true of systems that are not at standard state.)*

Practice Exercises

20.5 | Based only on the half-reactions in Table 20.1, determine what spontaneous reaction will occur if the following substances are mixed together: (a) I_2, I^- and Fe^{2+}, Fe^{3+}; (b) Mg, Mg^{2+} and Cr, Cr^{3+}; (c) Co, Co^{2+} and H_2SO_3, SO_4^{2-}. (*Hint*: Use Table 20.1 to write the possible half-reactions and, if necessary, determine $E°_{cell}$.)

20.6 | Use the positions of the half-reactions in Table 20.1 to predict the spontaneous reaction when Br^-, SO_4^{2-}, H_2SO_3, and Br_2 are mixed in an acidic solution at standard state.

20.7 | From the positions of the respective half-reactions in Table 20.1, predict whether the following reaction is spontaneous if all the ions are 1.0 *M* at 25 °C. If it is not, write the equation that represents a spontaneous reaction.

$$Ni^{2+}(aq) + 2Fe^{2+}(aq) \longrightarrow Ni(s) + 2Fe^{3+}(aq)$$

Calculating Standard Cell Potentials

We've just seen that we can use standard reduction potentials to predict spontaneous redox reactions. If we intend to use these reactions in a galvanic cell, we can also predict what the standard cell potential will be, as illustrated in the next example.

Example 20.4

Predicting the Cell Reaction and Standard Cell Potential of a Galvanic Cell

A typical cell of a lead storage battery of the type used to start automobiles is constructed using electrodes made of lead and lead(IV) oxide (PbO_2) and with sulfuric acid as the electrolyte. The half-reactions and their standard reduction potentials in this system are

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O \qquad E°_{PbO_2} = 1.69 \text{ V}$$

$$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq) \qquad E°_{PbSO_4} = -0.36 \text{ V}$$

What is the cell reaction and what is the standard potential of this cell?

Analysis: We can easily predict spontaneous reactions if the system is at standard state. In the spontaneous cell reaction, the half-reaction with the larger (more positive) standard reduction potential will take place as reduction while the other half-reaction will be reversed and occur as oxidation.

Assembling the Tools: The standard cell potential for a spontaneous reaction is simply the difference between the two standard reduction potentials, calculated using Equation 20.2, that results in a positive number. In this example we are given the standard reduction potentials. If they were not given, we would use a table of standard reduction potentials for the needed data.

We use the methods in Section 6.2 to combine the two half-reactions, once we determine which should be the oxidation and which is the reduction, based on which standard reduction potential is more positive.

Solution: PbO_2 has a larger, more positive standard reduction potential than $PbSO_4$, so the first half-reaction will occur in the direction written. The second must be reversed to occur as an oxidation. In the cell, therefore, the half-reactions are

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$$
$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

Since both half reactions have two electrons each, we can add the two half-reactions and cancel the electrons to obtain the cell reaction,

$$PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

The cell standard potential is

$$E^\circ_{\text{cell}} = (E^\circ \text{ of substance reduced}) - (E^\circ \text{ of substance oxidized})$$

Since the first half-reaction occurs as a reduction and the second as an oxidation,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{PbO_2} - E^\circ_{PbSO_4} \\ &= (1.69\text{ V}) - (-\ 0.36\text{ V}) \\ &= 2.05\text{ V} \end{aligned}$$

Are the Answer Reasonable? The half-reactions involved in the problem are located in Table 20.1, and their relative positions tell us that PbO_2 will be reduced and that lead will be oxidized. Therefore, we've combined the half-reactions correctly and we can feel confident that we've also applied Equation 20.2 correctly.

Remember that half-reactions are combined following the same procedure used in the ion–electron method of balancing redox reactions (Section 6.2).

Example 20.5

Predicting the Cell Reaction and Standard Cell Potential of a Galvanic Cell

A galvanic cell is constructed by placing 1.0 *M* aluminum nitrate in one beaker with an aluminum electrode and a second beaker with 1.0 *M* copper nitrate and a copper electrode. When a salt bridge is inserted to connect the two beakers, what cell potential do we expect to measure between the copper and aluminum electrodes? Which electrode is the anode and what is the spontaneous chemical reaction?

Analysis: This problem is very similar to the preceding one, so we expect to proceed in essentially the same way, but we have a bit more work to do. We need to write the correct formulas, ions, and possible half-reactions that are involved. Then we will use their standard reduction potentials to make appropriate decisions to arrive at the spontaneous reaction and standard cell potential.

Assembling the Tools: We will use the information in Section 6.2 to write the half reactions for each cell (review Section 3.5 for nomenclature if necessary). Next, the principles used previously will be used to correctly determine which should be the reduction half-reaction and which the oxidation half-reaction. This will also tell us which electrode is the cathode and which is the anode. Finally, we need Equation 20.2 to determine the standard cell voltage.

Solution: First, we will write two half-reactions (in the form of reduction half-reactions) for Cu^{2+} reduced to $Cu(s)$ and for Al^{3+} reduced to $Al(s)$. Our tool for predicting spontaneous reactions indicates that the half-reaction with the more positive standard reduction potential will occur as a reduction; the other will occur as an oxidation. In this cell, then, Cu^{2+} is reduced and Al is oxidized. To obtain the cell reaction, we add the two half-reactions, remembering that the electrons must cancel. This means we must multiply the copper half-reaction by 3 and the aluminum half-reaction by 2.

$$\begin{array}{rr} 3[\mathrm{Cu}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s)] & \text{(reduction)} \\ 2[\mathrm{Al}(s) \longrightarrow \mathrm{Al}^{3+}(aq) + 3e^-] & \text{(oxidation)} \\ \hline 3\mathrm{Cu}^{2+}(aq) + 2\mathrm{Al}(s) \longrightarrow 3\mathrm{Cu}(s) + 2\mathrm{Al}^{3+}(aq) & \text{(cell reaction)} \end{array}$$

The anode in the cell is aluminum because that is where oxidation takes place (by definition).

To obtain the standard cell potential, we substitute into Equation 20.2.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\mathrm{Cu}^{2+}} - E^\circ_{\mathrm{Al}^{3+}} \\ &= (0.34\ \mathrm{V}) - (-\ 1.66\ \mathrm{V}) \\ &= 2.00\ \mathrm{V} \end{aligned}$$

An important point to notice here is that *although we multiply the half-reactions by factors to make the electrons cancel,* ***we do not multiply the standard reduction potentials by these factors***.[3] To obtain the standard cell potential, we simply subtract one standard reduction potential from the other.

■ **Are the Answers Reasonable?** If we locate these half-reactions in Table 20.1, their relative positions tell us we've written the correct equation for the spontaneous reaction. It also means we've identified correctly the substances reduced and oxidized, so we've correctly applied Equation 20.2.

Practice Exercises

■ These are the reactions in an Edison cell, a type of rechargeable storage battery.

20.8 | What are the overall cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions?

$$\begin{array}{rr} \mathrm{NiO_2}(s) + 2\mathrm{H_2O} + 2e^- \rightleftharpoons \mathrm{Ni(OH)_2}(s) + 2\mathrm{OH}^-(aq) & E^\circ_{\mathrm{NiO_2}} = 0.49\ \mathrm{V} \\ \mathrm{Fe(OH)_2}(s) + 2e^- \rightleftharpoons \mathrm{Fe}(s) + 2\mathrm{OH}^-(aq) & E^\circ_{\mathrm{Fe(OH)_2}} = -0.88\ \mathrm{V} \end{array}$$

(*Hint*: Recall that standard cell potentials are based on a spontaneous reaction.)

20.9 | What are the overall cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions?

$$\begin{array}{rr} \mathrm{Cr}^{3+}(aq) + 3e^- \rightleftharpoons \mathrm{Cr}(s) & E^\circ_{\mathrm{Cr}^{3+}} = -0.74\ \mathrm{V} \\ \mathrm{MnO_4}^-(aq) + 8\mathrm{H}^+(aq) + 5e^- \rightleftharpoons \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O} & E^\circ_{\mathrm{MnO_4}^-} = +1.51\ \mathrm{V} \end{array}$$

20.10 | A 1.0 *M* solution of copper perchlorate and 1.0 *M* chromium(III) nitrate along with some copper wire and a chunk of chromium are placed in the same beaker, at 25 °C. Write the balanced equation for the spontaneous reaction, and determine the standard cell potential if the same materials are used in a galvanic cell.

Cell Potentials of Spontaneous Reactions

Because we can predict the spontaneous redox reaction that will take place among a mixture of reactants, it also should be possible to predict whether or not a particular reaction, *as written*, can occur spontaneously. We can do this by calculating the standard cell potential that corresponds to the reaction in question and seeing if the standard potential is *positive.*

TOOLS

E°_{cell} and spontaneous reactions

> In a galvanic cell, the calculated standard cell potential for the spontaneous reaction is always positive. If the calculated standard cell potential is negative, the reaction is spontaneous in the reverse direction.

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[3] Reduction potentials are intensive quantities; they have the units volts, which are joules *per coulomb*. The same number of joules are available for each coulomb of charge regardless of the total number of electrons shown in the equation. Therefore, reduction potentials are never multiplied by factors before they are subtracted to give the cell potential.

For example, to obtain the standard cell potential for a spontaneous reaction in our previous examples, we subtracted the standard reduction potentials in a way that gave a positive answer. Therefore, if we compute the standard cell potential for a particular reaction *based on the way the equation is written* and the standard potential comes out positive, we know the reaction is spontaneous. If the calculated standard cell potential comes out negative, however, the reaction is nonspontaneous. In fact, it is really spontaneous in the opposite direction.

Example 20.6

Determining Whether a Reaction Is Spontaneous by Using the Calculated Standard Cell Potential

Determine whether the following reactions, at standard state, are spontaneous as written. If a reaction is not spontaneous, write the equation for the reaction that is.

$$(1)\quad Cu(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$$

$$(2)\quad 3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O$$

Analysis: Our goal for each reaction will be to calculate the standard cell potential based on the reaction as written. Based on that we will determine if the reaction as written is spontaneous. If the reaction is not spontaneous, we will write the reverse reaction, which will be spontaneous.

Assembling the Tools: The algebraic sign of E°_{cell} will tell us if a reaction as written is spontaneous. To calculate E°_{cell}, we need to divide the equation into its half-reactions (Chapter 6), find the necessary standard reduction potentials in Table 20.1, and then use Equation 20.2 to calculate E°_{cell}. The signs of E°_{cell} will then tell us whether or not the reactions are spontaneous as written under standard conditions.

Solution: (1) The half-reactions involved in this equation are

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad \text{(reduction)}$$

The H^+ is reduced and Cu is oxidized, so Equation 20.2 will take the form

$$E^\circ_{cell} = \underset{\substack{\uparrow \\ \text{Standard reduction} \\ \text{potential of substance} \\ \text{reduced}}}{E^\circ_{H^+}} - \underset{\substack{\uparrow \\ \text{Standard reduction} \\ \text{potential of substance} \\ \text{oxidized}}}{E^\circ_{Cu^{2+}}}$$

Substituting values from Table 20.1 gives

$$\begin{aligned} E^\circ_{cell} &= (0.00\text{ V}) - (0.34\text{ V}) \\ &= -0.34\text{ V} \end{aligned}$$

The calculated standard cell potential is negative, so reaction (1) is not spontaneous in the forward direction. The spontaneous reaction is actually the reverse of (1).

$$\underset{\text{Reaction (1) reversed}}{Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)}$$

(2) The half-reactions involved in this equation are

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$$

The Cu is oxidized while the NO_3^- is reduced. According to Equation 20.2,

$$E^\circ_{\text{cell}} = E^\circ_{NO_3^-} - E^\circ_{Cu^{2+}}$$

Substituting values from Table 20.1 gives

$$\begin{aligned} E^\circ_{\text{cell}} &= (0.96 \text{ V}) - (0.34 \text{ V}) \\ &= +0.62 \text{ V} \end{aligned}$$

■ Copper dissolves in HNO_3 because it contains the oxidizing agent NO_3^-.

Because the calculated standard cell potential is positive, reaction (2) is spontaneous in the forward direction, as written.

■ **Are the Answers Reasonable?** By noting the relative positions of the half-reactions in Table 20.1, you can confirm that we've answered the questions correctly.

Practice Exercises

20.11 | Write each of the following equations so that they represent spontaneous reactions at standard state.

(a) $Br_2(aq) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$

(b) $MnO_4^-(aq) + 5Ag(s) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Ag^+(aq) + 4H_2O$

(*Hint:* Determine the sign of the calculated standard cell potential.)

20.12 | Under standard state conditions, which of the following reactions occur spontaneously? Justify your answer.

(a) $Br_2(aq) + Cl_2(g) + 2H_2O \longrightarrow 2Br^-(aq) + 2HOCl(aq) + 2H^+(aq)$

(b) $3Zn(s) + 2Cr^{3+}(aq) \longrightarrow 3Zn^{2+}(aq) + 2Cr(s)$

In the previous examples and exercises we have been rigorous in specifying that standard reduction potentials are used when the system is at standard state. If the cell is not at standard state, the numerical value of the cell potential, E_{cell}, will not be the same as the standard cell potential, but in the majority of cases, the algebraic sign of E_{cell} will be the same and we can reach the same conclusions about spontaneity. We will consider methods for computing E_{cell} in Section 20.5.

20.4 | E°_{cell} and ΔG°

The fact that cell potentials allow us to predict the spontaneity of redox reactions is no coincidence. There is a relationship between the cell potential and the free energy change for a reaction. In Chapter 19, we saw that ΔG for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction. Specifically, the relationship is

$$-\Delta G = \text{maximum work} \qquad \textbf{(20.3)}$$

In an electrical system, work is supplied by the flow of electric charge created by the potential of the cell. It can be calculated from the equation

TOOLS

Faraday constant

$$\text{maximum work} = n\mathcal{F}E_{\text{cell}} \qquad \textbf{(20.4)}$$

■ More precisely, 1 $\mathcal{F}$ = 96,485 C.

where n is the number of moles of electrons transferred, $\mathcal{F}$ is a constant called the **Faraday constant,** which is equal to the number of coulombs of charge equivalent to 1 mol of electrons (9.65×10^4 coulombs per mole of electrons), and E_{cell} is the potential of the cell in volts. To see that Equation 20.4 gives work (which has the units of energy) we can analyze the units. In Equation 20.1 you saw that 1 volt = 1 joule/coulomb. Therefore,

$$\text{maximum work} = \underset{\displaystyle n}{\underset{\Updownarrow}{\cancel{\text{mole}}\ \text{e}^-}} \times \underset{\displaystyle \mathcal{F}}{\underset{\Updownarrow}{\left(\frac{\cancel{\text{coulombs}}}{\cancel{\text{mole e}^-}}\right)}} \times \underset{\displaystyle E_\text{cell}}{\underset{\Updownarrow}{\left(\frac{\text{joule}}{\cancel{\text{coulombs}}}\right)}} = \text{joule}$$

Combining Equations 20.3 and 20.4 gives us

$$\Delta G = -n\,\mathcal{F}E_\text{cell} \tag{20.5}$$

ΔG related to E_cell

At standard state we are dealing with the *standard* cell potential, so we can calculate the *standard* free energy change.

$$\Delta G^\circ = -n\,\mathcal{F}E^\circ_\text{cell} \tag{20.6}$$

ΔG° related to E°_cell

Referring back to Chapter 19, if ΔG has a negative value, a reaction will be spontaneous, and this corresponds to a positive value of E_cell.

Up to now we have been careful to predict spontaneity for systems at standard state where E_cell is equal to E°_cell. Later in Section 20.5, we will see how to calculate E_cell under nonstandard state conditions and precisely predict if a reaction is spontaneous.

Example 20.7
Calculating the Standard Free Energy Change

Calculate ΔG° for the following reaction, given that its standard cell potential is 0.320 V at 25 °C.

$$\text{NiO}_2(s) + 2\text{Cl}^-(aq) + 4\text{H}^+(aq) \longrightarrow \text{Cl}_2(g) + \text{Ni}^{2+}(aq) + 2\text{H}_2\text{O}$$

Analysis: We will need to use the relationship between E°_cell and ΔG°. The given chemical equation allows us to determine n, which is used in the equation.

Assembling the Tools: Our tool for solving this problem is Equation 20.6.

$$\Delta G^\circ = -n\,\mathcal{F}E^\circ_\text{cell}$$

We know $\mathcal{F}$ and E°_cell, and the value of n, the total number of electrons transferred in the balanced chemical equation, can be computed with the aid of principles developed in Section 6.2. We will also use the Faraday constant, $1\ \mathcal{F} = 9.65 \times 10^4$ C/mol e^- (the SI abbreviation for coulomb is C).

$$1\ \mathcal{F} = \left(\frac{9.65 \times 10^4\ \text{C}}{1\ \text{mol}\ e^-}\right)$$

Solution: To solve Equation 20.6 we need to determine n. By taking the coefficients in the chemical equation to stand for *moles*, two moles of Cl^- are oxidized to Cl_2 and two moles of electrons are transferred to the NiO_2. Therefore we conclude that $n = 2$ mol e^-. Using Equation 20.6, we have

$$\begin{aligned}\Delta G^\circ &= -(2\ \cancel{\text{mol}\ e^-}) \times \left(\frac{9.65 \times 10^4\ \cancel{\text{C}}}{1\ \cancel{\text{mol}\ e^-}}\right) \times \left(\frac{0.320\ \text{J}}{\cancel{\text{C}}}\right)\\ &= -6.18 \times 10^4\ \text{J}\\ &= -61.8\ \text{kJ}\end{aligned}$$

Is the Answer Reasonable? Let's do some approximate arithmetic. The Faraday constant equals approximately 100,000, or 10^5. The product $2 \times 0.32 = 0.64$, so ΔG° should be about 0.64×10^5 or 6.4×10^4. The answer seems to be okay. Importantly, the algebraic signs tell us the same thing: that is, the positive E°_cell and the negative ΔG° both predict a spontaneous reaction.

Practice Exercises

20.13 | A certain reaction has an E°_{cell} of 0.107 volts and has a ΔG° of -30.9 kJ. How many electrons are transferred in the reaction? (*Hint*: See Equation 20.6.)

20.14 | Calculate ΔG° for the reactions that take place in the galvanic cells described in Practice Exercises 20.11 and 20.12.

E°_{cell} and Equilibrium Constants

One of the useful applications of electrochemistry is the determination of equilibrium constants. In Chapter 19 you saw that ΔG° is related to the equilibrium constant by the expression

$$\Delta G^\circ = -RT \ln K_c$$

where we used K_c for the equilibrium constant because electrochemical reactions occur in solution. Earlier in this section we saw that ΔG° is also related to E°_{cell}

$$\Delta G^\circ = -n \mathscr{F} E^\circ_{\text{cell}}$$

Therefore, E°_{cell} and the equilibrium constant are also related. Equating the right sides of the two equations, we have

$$-n \mathscr{F} E^\circ_{\text{cell}} = -RT \ln K_c$$

Solving for E°_{cell} gives[4]

K_c related to E°_{cell}

$$E^\circ_{\text{cell}} = \frac{RT}{n \mathscr{F}} \ln K_c \qquad \textbf{(20.7)}$$

For the units to work out correctly, the value of R must be 8.314 J mol^{-1} K^{-1}, T must be the temperature in kelvins, $\mathscr{F}$ equals 9.65×10^4 C per mole of e^-, and n equals the number of moles of electrons transferred in the reaction.

Example 20.8
Calculating Equilibrium Constants from E°_{cell}

Calculate K_c for the reaction in Example 20.7.

Analysis: We now have an equation that relates the standard cell potential and the equilibrium constant. We need to choose the appropriate values for each variable to determine K_c.

Assembling the Tools: Equation 20.7 is our tool for solving this problem. We need to collect the terms to insert in this equation to solve it. We need to find E°_{cell}, n, R, T, and $\mathscr{F}$. Remember that T is in kelvins and R must have the appropriate units of J mol^{-1} K^{-1}. Collecting the values needed, we find:

$T = 25\ ^\circ\text{C} = 298$ K

$\mathscr{F} = 9.65 \times 10^4$ C per mole of e^-

$R = 8.314$ J mol^{-1} K^{-1}

$E^\circ_{\text{cell}} = 0.320\ \text{V} = 0.320\ \text{J C}^{-1}$

$n = 2$

---

[4] For historical reasons, Equation 20.7 is sometimes expressed in terms of common logs (base 10 logarithms). Natural and common logarithms are related by the equation

$$\ln x = 2.303 \log x$$

For reactions at 25 °C (298 K), all of the constants (R, T, and $\mathscr{F}$) can be combined with the factor 2.303 to give 0.0592 joules/coulomb. Because joules/coulomb equals volts, Equation 20.7 reduces to

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n} \log K_c$$

where n is the number of moles of electrons transferred in the cell reaction as it is written.

Solution: With all of the data, let's rearrange Equation 20.7 for ln K_c and then substitute values.

$$\ln K_c = \frac{E^\circ_{\text{cell}}\, n\, \mathcal{F}}{RT}$$

Substituting values,

$$\begin{aligned}\ln K_c &= \frac{0.320\ \cancel{\text{J}}\ \cancel{\text{C}^{-1}} \times 2 \times 9.65 \times 10^4\ \cancel{\text{C}}\ \cancel{\text{mol}^{-1}}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298\ \cancel{\text{K}}}\\ &= 24.9\end{aligned}$$

Taking the antilogarithm,

$$K_c = e^{24.9} = 7 \times 10^{10}$$

Is the Answer Reasonable? As a rough check, we can look at the magnitude of E°_{cell} and apply some simple reasoning. When E°_{cell} is positive, ΔG° is negative, and in Chapter 19 you learned that when ΔG° is negative, the position of equilibrium lies toward the product side of the reaction. Therefore, we expect that K_c will be large, and that agrees with our answer.

A more complete check would require evaluating the fraction used to compute ln K_c. First, we should check to be sure we've substituted correctly into the equation for ln K_c. Next, we could do some approximate arithmetic to check the value of ln K_c. Rounding all numbers to one significant figure we get:

$$\ln K_c = \frac{0.3\ \cancel{\text{J}}\ \cancel{\text{C}^{-1}} \times 2 \times 10 \times 10^4\ \cancel{\text{C}}\ \cancel{\text{mol}^{-1}}}{10\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 300\ \cancel{\text{K}}} = \frac{6 \times 10^4}{3000} = 2 \times 10^1 = 20$$

This is close to the 24.9 we calculated above, and we are confident the calculation was done correctly.

Practice Exercises

20.15 | The calculated standard cell potential for the reaction

$$\text{Cu}^{2+}(aq) + 2\text{Ag}(s) \rightleftharpoons \text{Cu}(s) + 2\text{Ag}^{+}(aq)$$

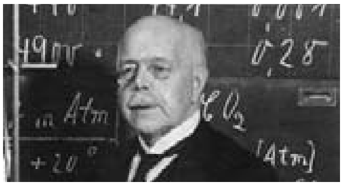
is $E^\circ_{\text{cell}} = -0.46$ V. Calculate K_c for this reaction as written. Is this reaction spontaneous? If not, what is K_c for the spontaneous reaction? (*Hint*: The tool described by Equation 20.7 is important here.)

20.16 | Use the following half-reactions and the data in Table 20.1 to write the spontaneous reaction. Write the equilibrium law for this reaction and use the standard cell voltage to determine the value of the equilibrium constant.

$$\text{Ag}^{+}(aq) + e^{-} \longrightarrow \text{Ag}(s)$$
$$\text{AgBr}(s) + e^{-} \longrightarrow \text{Ag}(s) + \text{Br}^{-}(aq)$$

20.5 | Cell Potentials and Concentrations

At 25 °C when all of the ion concentrations in a cell are 1.00 *M* and when the partial pressures of any gases involved in the cell reaction are 1.00 atm, the cell potential is equal to the standard potential. When the concentrations or pressures change, however, so does the potential. For example, in an operating cell or battery, the potential gradually drops as the reactants are used up and as the cell reaction approaches its natural equilibrium status. When it reaches equilibrium, the potential has dropped to zero—the battery is "dead".



Walther Nernst (1864–1941) was a professor of physical chemistry who developed the equation named after him. *(Ullstein Bild/The Granger Collection, New York)*

TOOLS

Nernst equation

The Nernst Equation

The effect of concentration on the cell potential can be obtained from thermodynamics. In Chapter 19, you learned that the free energy change is related to the reaction quotient Q by the equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Substituting for ΔG and ΔG° from Equations 20.5 and 20.6 gives

$$-n\mathscr{F}E_{\text{cell}} = -n\mathscr{F}E^\circ_{\text{cell}} + RT \ln Q$$

Dividing both sides by $-n\mathscr{F}$ gives

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln Q \qquad \textbf{(20.8)}$$

This equation is commonly known as the **Nernst equation,**[5] named after Walther Nernst, a German chemist and physicist. Notice that if $Q = 1$, then $\ln Q = 0$ and $E_{\text{cell}} = E^\circ{}_{\text{cell}}$.

In writing the Nernst equation for a galvanic cell, we will construct the mass action expression (from which we calculate the value of Q) using molar concentrations for ions and partial pressures in atmospheres for gases.[6] Thus, for the following cell using a hydrogen electrode (with the partial pressure of H_2 not necessarily equal to 1 atm) and having the reaction

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

the Nernst equation would be written

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln \frac{[H^+]^2}{[Cu^{2+}]\,P_{H_2}}$$

This is a heterogeneous reaction, so we have not included the concentration of the solid, Cu(s), in the mass action expression.

Example 20.9

Calculating the Effect of Concentration on E_{cell}

Suppose a galvanic cell employs the following half-reactions.

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E^\circ_{Ni^{2+}} = -0.25\text{ V}$$
$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \qquad E^\circ_{Cr^{3+}} = -0.74\text{ V}$$

Calculate the cell potential when $[Ni^{2+}] = 4.87 \times 10^{-4}\,M$ and $[Cr^{3+}] = 2.48 \times 10^{-3}\,M$.

Analysis: We will be calculating the cell potential for a system that does not have standard state concentrations by using the Nernst equation. As with previous problems, we will need to write the appropriate chemical equations so that the variables can be identified and used properly.

Assembling the Tools: We start with the Nernst equation, Equation 20.8, to determine E_{cell}.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln Q$$

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[5] Using common logarithms instead of natural logarithms and calculating the constants for 25 °C gives another form of the Nernst equation that is sometimes used:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\text{ V}}{n} \log Q$$

[6] Because of interionic attractions, ions do not always behave as though their concentrations are equal to their molarities. Strictly speaking, therefore, we should use effective concentrations (called activities) in the mass action expression. Effective concentrations are difficult to calculate, so for simplicity we will use molarities and accept the fact that our calculations are not entirely accurate.

The balanced chemical equation is needed (Chapter 6) to determine the number of electrons transferred, *n*, and the correct form of the mass action expression (Chapter 15) from which we calculate the value of *Q*.

■ **Solution:** Nickel has the more positive (less negative) standard reduction potential, so its half-reaction will occur as a reduction. This means that chromium will be oxidized. Making electron gain ($6e^-$) equal to electron loss ($6e^-$), the cell reaction is found as follows.

$$\begin{array}{rr} 3[\mathrm{Ni}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Ni}(s)] & \text{(reduction)} \\ 2[\mathrm{Cr}(s) \longrightarrow \mathrm{Cr}^{3+}(aq) + 3e^-] & \text{(oxidation)} \\ \hline 3\mathrm{Ni}^{2+}(aq) + 2\mathrm{Cr}(s) \longrightarrow 3\mathrm{Ni}(s) + 2\mathrm{Cr}^{3+}(aq) & \text{(cell reaction)} \end{array}$$

The total number of electrons transferred is six, which means $n = 6$. Now we can write the Nernst equation for the system.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln \frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Ni}^{2+}]^3}$$

Notice that we've constructed the mass action expression, from which we will calculate the reaction quotient, using the concentrations of the ions raised to powers equal to their coefficients in the net cell reaction, and that we have not included concentration terms for the two solids. This is the procedure we followed for heterogeneous equilibria in Section 15.4.

Next we need E°_{cell}. Since Ni^{2+} is reduced,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\mathrm{Ni}^{2+}} - E^\circ_{\mathrm{Cr}^{3+}} \\ &= (-0.25\ \mathrm{V}) - (-0.74\ \mathrm{V}) \\ &= 0.49\ \mathrm{V} \end{aligned}$$

Now we can substitute this value for E°_{cell} along with $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $T = 298\ \mathrm{K}$, $n = 6$, $\mathscr{F} = 9.65 \times 10^4\ \mathrm{C\ mol^{-1}}$, $[\mathrm{Ni}^{2+}] = 4.87 \times 10^{-4}\ M$, and $[\mathrm{Cr}^{3+}] = 2.48 \times 10^{-3}\ M$ into the Nernst equation. This gives

$$E_{\text{cell}} = 0.49\ \mathrm{V} - \frac{8.314\ \mathrm{J}\ \cancel{\mathrm{mol}^{-1}}\ \cancel{\mathrm{K}^{-1}} \times 298\ \cancel{\mathrm{K}}}{6 \times (9.65 \times 10^4\ \mathrm{C}\ \cancel{\mathrm{mol}^{-1}})} \ln \frac{(2.48 \times 10^{-3})^2}{(4.87 \times 10^{-4})^3}$$

We notice that the volt, V, is 1 J/C so that we obtain

$$\begin{aligned} E_{\text{cell}} &= 0.49\ \mathrm{V} - (0.00428\ \mathrm{V}) \ln (5.32 \times 10^4) \\ &= 0.49\ \mathrm{V} - (0.00428\ \mathrm{V})\ (10.882) \\ &= 0.49\ \mathrm{V} - 0.0525\ \mathrm{V} \\ &= 0.44\ \mathrm{V} \end{aligned}$$

The potential of the cell is expected to be 0.44 V.

■ **Is the Answer Reasonable?** There's no simple way to check the answer, but the small numerical value of 0.44 V is reasonable. In addition, there are certain important points to consider. First, check that you've combined the half-reactions correctly to (a) calculate E°_{cell} and (b) give the balanced cell reaction. Now check that we wrote the correct mass action expression from the balanced equation and that we have the correct number of electrons transferred, *n*. Finally, check that the Kelvin temperature and $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$ were used.

Example 20.10
The Spontaneous Reaction May Be Concentration Dependent

The reaction of tin metal with acid can be written as

$$\mathrm{Sn}(s) + 2\mathrm{H}^+(aq) \longrightarrow \mathrm{Sn}^{2+}(aq) + \mathrm{H}_2(g)$$

Calculate the cell potential when (a) the system is at standard state, (b) the pH is 2.00, and (c) the pH is 5.00. Assume that $[\mathrm{Sn}^{2+}] = 1.0\ M$ and the partial pressure of H_2 is 1.00 atm.

Analysis: We will be using the equations developed in this chapter for computing the values for the standard cell potential and various cell potentials. For this we will need to identify the substances that are oxidized and reduced in a chemical reaction and gather the information needed to solve the appropriate equations. One way to approach this problem is to write out the equations and then find values for the variables.

Assembling the Tools: Part (a) is at standard state, and we have used Equation 20.2 for combining standard reduction potentials to solve problems like that in Examples 20.5 and 20.6. In this reaction we identify the tin metal as the substance that is oxidized and hydrogen ions are reduced.

For parts (b) and (c) we must use the Nernst equation as our tool, Equation 20.8. We determine the number of electrons transferred, *n*, by noting that tin loses two electrons and each hydrogen gains an electron. Therefore two electrons are transferred from tin to the hydrogen ions. We can also set up *Q*, see Chapter 15, for the Nernst equation. Substituting 1.00 for both $[\text{Sn}^{2+}]$ and P_{H_2}, the result is

$$Q = \frac{[\text{Sn}^{2+}]\,P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{1}{[\text{H}^+]^2}$$

We can also calculate the hydrogen ion concentrations for the pH 2.00 and pH 5.00 solutions as $1.0 \times 10^{-2}\ M$ and $1.0 \times 10^{-5}\ M$, respectively.

Solution: For part (a) we find the difference between standard reduction potentials as

$$E^\circ_{\text{cell}} = 0.00 - (-0.14) = +0.14\text{ V}$$

For parts (b) and (c) we substitute into the Nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln \frac{1}{[\text{H}^+]^2}$$

$$\text{(b) } E_{\text{cell}} = 0.14\text{ V} - \frac{8.314\text{ J }\cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298\ \cancel{\text{K}}}{2 \times (9.65 \times 10^{4}\text{ C }\cancel{\text{mol}^{-1}})} \ln \frac{1}{(1.0 \times 10^{-2})^2}$$

$$E_{\text{cell}} = 0.14\text{ V} - 0.12 = +0.02\text{ V}$$

$$\text{(c) } E_{\text{cell}} = 0.14\text{ V} - \frac{8.314\text{ J }\cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298\ \cancel{\text{K}}}{2 \times (9.65 \times 10^{4}\text{ C }\cancel{\text{mol}^{-1}})} \ln \frac{1}{(1.0 \times 10^{-5})^2}$$

$$E_{\text{cell}} = 0.14\text{ V} - 0.30 = -0.16\text{ V}$$

At standard state the reaction is spontaneous, and at pH = 2.00 it is spontaneous, but the potential is barely positive. At pH 5.00 the reaction is not spontaneous, but the reverse reaction will be.

Is the Answer Reasonable? The first question to answer is "does this make sense?" and indeed it does. Looking at the natural logarithm part of the equation we see that as the $[\text{H}^+]$ decreases, the ln term increases and makes a more negative adjustment to the E°_{cell}. Since a decrease in $[\text{H}^+]$ is an increase in pH, we expect E_{cell} will decrease as pH increases. We cannot easily estimate natural logarithms, so a check of calculations may be easiest if the values are entered into your calculator in a different sequence from your first calculation.

Practice Exercises

20.17 | A galvanic cell is constructed with a copper electrode dipping into a 0.015 *M* solution of Cu^{2+} ions and an electrode made of magnesium is immersed in a $2.2 \times 10^{-6}\ M$ solution of magnesium ions. What is the balanced chemical equation and the cell potential at 25 °C? (*Hint*: Set up the Nernst equation for this reaction.)

20.18 | In Example 20.10, assume all conditions are the same except for the pH. At what pH will the cell potential be zero?

20.19 | In a certain zinc–copper cell,

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

the ion concentrations are $[\text{Cu}^{2+}] = 0.0100\ M$ and $[\text{Zn}^{2+}] = 1.0\ M$. What is the cell potential at 25 °C?

Concentration from E_{cell} Measurements

One of the principal uses of the relationship between concentration and cell potential is for the measurement of concentrations of redox reactants and products in a galvanic cell. Experimental determination of cell potentials combined with modern developments in electronics has provided a means of monitoring and analyzing the concentrations of all sorts of substances in solution, even some that are not themselves ionic and that are not involved directly in electrochemical changes. In fact, the operation of a pH meter relies on the logarithmic relationship between hydrogen ion concentration and the potential of a special kind of electrode (Figure 20.8).

■ The ease of such operations and the fact that they lend themselves well to automation and computer analysis make electrochemical analyses especially attractive to scientists.

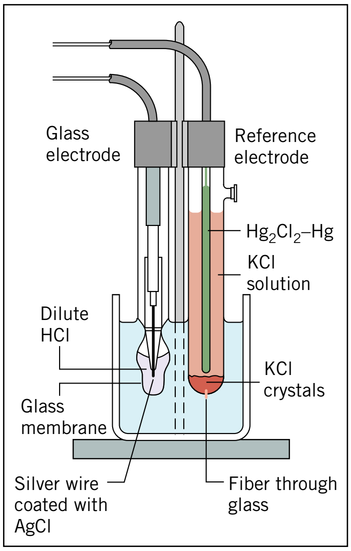


Figure 20.8 | **Electrodes used with a pH meter.** The electrode on the left is called a *glass electrode*. It contains a silver wire, coated with AgCl, dipping into a dilute solution of HCl. This half-cell has a potential that depends on the difference between the [H^+] inside and outside a thin glass membrane at the bottom of the electrode. On the right is a reference electrode that forms the other half-cell. The galvanic cell formed by the two electrodes produces a potential that is proportional to the pH of the solution into which they are dipped.

Example 20.11

Using the Nernst Equation to Determine Concentrations

A laboratory was assigned the job of determining the copper(II) ion concentration in thousands of water samples. To make these measurements an electrochemical cell was assembled that consists of a silver electrode, dipping into a 0.225 M solution of $AgNO_3$, connected by a salt bridge to a second half-cell containing a copper electrode. The copper half-cell was then filled with one water sample after another, with the cell potential measured for each sample. In the analysis of one sample, the cell potential at 25 °C was measured to be 0.62 V. The copper electrode was observed to carry a negative charge, so it served as the anode. What was the concentration of copper ion in this sample?

■ **Analysis:** In this problem, we've been given the cell potential, E_{cell}, and we can calculate E°_{cell}. The unknown quantity is one of the concentration terms in Q that is part of the Nernst equation. Once we assemble all of the variables for the Nernst equation, an algebraic solution is possible.

■ **Assembling the Tools:** We will need Equation 20.8, the Nernst equation, and the chemical reaction represented by the description of the galvanic cell. Because copper is the anode, it is being oxidized. This also means that Ag^+ is being reduced. Therefore, the equation for the cell reaction is

$$\text{Cu}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s)$$

From the balanced equation we can determine the mass action expression, n, and E°_{cell}. Since R and Faraday's constant are known, along with the concentration of silver ions, the remaining variable is [Cu^{2+}] that the question asks us to compute.

Solution: Two electrons are transferred, so $n = 2$ and the Nernst equation is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{2\,\mathcal{F}} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$$

The value of E°_{cell} can be obtained from the tabulated standard reduction potentials in Table 20.1. Following our usual procedure and recognizing that silver ion is reduced,

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Ag}^+} - E^{\circ}_{\text{Cu}^{2+}} \\ &= (0.80 \text{ V}) - (0.34 \text{ V}) \\ &= 0.46 \text{ V} \end{aligned}$$

Now we can substitute values into the Nernst equation and solve for the concentration ratio in the mass action expression.

$$0.62 \text{ V} = 0.46 \text{ V} - \frac{8.314 \text{ J } \cancel{\text{mol}^{-1}} \ \cancel{\text{K}^{-1}} \times 298 \ \cancel{\text{K}}}{2 \times \left(9.65 \times 10^4 \text{ C } \cancel{\text{mol}^{-1}}\right)} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$$

Solving for ln $([\text{Cu}^{2+}]/[\text{Ag}^{+}]^2)$ gives (retaining one extra significant figure)

$$\ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2} = -12.5$$

Taking the antilog gives us the value of the mass action expression.

$$\frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2} = 4 \times 10^{-6}$$

Since we know that the concentration of Ag^+ is 0.225 *M*, we can now solve for the Cu^{2+} concentration.

$$\frac{[\text{Cu}^{2+}]}{(0.225)^2} = 4 \times 10^{-6}$$

$$[\text{Cu}^{2+}] = 2 \times 10^{-7} \ M \ \text{(correctly rounded)}$$

Is the Answer Reasonable? All we can do easily is check to be sure we've written the correct chemical equation, on which all the rest of the solution to the problem rests. Be careful about algebraic signs and that you select the proper value for R and the temperature in kelvins. Also, notice that we first solved for the logarithm of the ratio of concentration terms. Then, after taking the (natural) antilogarithm, we substitute the known value for $[\text{Ag}^+]$ and solve for $[\text{Cu}^{2+}]$.

As a final point, notice that the Cu^{2+} concentration is indeed very small, and that it can be obtained very easily by simply measuring the potential generated by the electrochemical cell. Determining the concentrations in many samples is also very simple—just change the water sample and measure the potential again.

Practice Exercises

20.20 | A galvanic cell is constructed with a copper electrode dipping into a 0.015 *M* solution of Cu^{2+} ions, and a magnesium electrode immersed in a solution with an unknown concentration of magnesium ions. The cell potential is measured as 2.79 volts at 25 °C. What is the concentration of magnesium ions?

$$\text{Mg}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$$

(*Hint:* Use the Nernst equation to solve for $[\text{Mg}^{2+}]$.)

20.21 | In the analysis of two other water samples by the procedure described in Example 20.11, cell potentials (E_{cell}) of 0.57 V and 0.82 V were obtained. Calculate the Cu^{2+} ion concentration in each of these samples.

20.22 | A galvanic cell was constructed with a nickel electrode that was dipped into 1.20 *M* NiSO_4 solution and a chromium electrode that was immersed into a solution containing Cr^{3+} at an unknown concentration. The potential of the cell was measured to be 0.552 V, with the chromium serving as the anode. The standard cell potential for this system was determined to be 0.487 V. What was the concentration of Cr^{3+} in the solution of unknown concentration?

Concentration Cells

The dependence of cell potential on concentration allows us to construct a galvanic cell from two half-cells composed of the same substances, but having different concentrations of the solute species. An example would be a pair of copper electrodes dipping into solutions that have different concentrations of Cu^{2+}, say 0.10 *M* Cu^{2+} in one and 1.0 *M* in the other (Figure 20.9). When this cell operates, reactions take place that tend to bring the two Cu^{2+} concentrations toward the same value. Thus, in the half-cell containing 0.10 *M* Cu^{2+}, copper is oxidized, which adds Cu^{2+} to the more dilute solution. In the other cell, Cu^{2+} is reduced, removing Cu^{2+} from the more concentrated solution. This makes the more dilute half-cell the anode and the more concentrated half-cell the cathode.

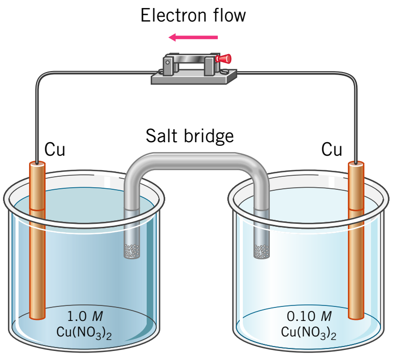


Figure 20.9 | **A concentration cell.** When the circuit is completed, reactions occur that tend to make the concentrations of Cu^{2+} the same in the two half-cells. Oxidation occurs in the more dilute half-cell, and reduction occurs in the more concentrated one.

$$\underset{\text{anode}}{Cu(s)\,|\,Cu^{2+}(0.10\,M)}\ \|\ \underset{\text{cathode}}{Cu^{2+}(1.0\,M)\,|\,Cu(s)}$$

The half-reactions in the spontaneous cell reaction are

$$\begin{array}{r}
Cu(s) \longrightarrow Cu^{2+}(0.10\,M) + 2e^- \\
Cu^{2+}(1.0\,M) + 2e^- \longrightarrow Cu(s) \\
\hline
Cu^{2+}(1.0\,M) \longrightarrow Cu^{2+}(0.10\,M)
\end{array}$$

The Nernst equation for this cell is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln \frac{[Cu^{2+}]_{\text{dilute}}}{[Cu^{2+}]_{\text{conc}}}$$

Because we're dealing with the same substances in the cell, $E^\circ_{\text{cell}} = 0$ V. When the cell operates, $n = 2$, and we'll take $T = 298$ K. Substituting values,

$$\begin{aligned}
E_{\text{cell}} &= 0\text{ V} - \frac{8.314\text{ J }\cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298\ \cancel{\text{K}}}{2 \times 9.65 \times 10^4\text{ C }\cancel{\text{mol}^{-1}}} \ln\left(\frac{0.10}{1.0}\right) \\
&= 0.030\text{ V}
\end{aligned}$$

In this concentration cell, one solution is ten times more concentrated than the other, yet the potential generated is only 0.03 V. In general, the potential generated by concentration differences are quite small. Yet they are significant in biological systems, where electrical potentials are generated across biological membranes by differences in ion concentrations (e.g., K^+). Membrane potentials are important in processes such as the transmission of nerve impulses.

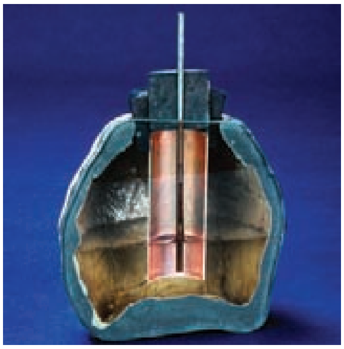
These small differences in potential also illustrate that if *Q*, in a system that is not at standard state, is between 0.10 and 10 we can conclude that $E_{\text{cell}} \approx E^\circ_{\text{cell}}$ and we can generalize the results in Sections 20.2 and 20.3 when predicting spontaneous reactions.

20.6 | Electricity

Large amounts of electricity are generated mechanically by rotating coils of wire in a magnetic field in a turbine. To rotate the coils, superheated steam, flowing water, and the wind are used in a variety of turbine designs. Superheated steam is produced reliably by burning coal, oil, natural gas, and even municipal wastes. Such turbines are used mainly in large central electrical generators near major population centers. Since the energy of the fuel is not completely converted into electricity, the efficiency of these generators ranges from 35 to 45% and they require a significant investment in pollution control.

Hydroelectric power plants are claimed to have efficiencies around 90%. They are clean and non-polluting. However, hydroelectric power often requires building large dams to maintain a reservoir of water. Additionally they are often located large distances from their customers, and transmission of electricity over long distances incurs significant losses. Wind powered turbines and wind mills are also considered to be clean and non-polluting. They are approximately 50% efficient and can be located very close to the end-user. However, daily, even hourly, fluctuations in wind speed may introduce inconvenient variations in power production.

Chemical research is important in producing new turbine materials and combustion processes to increase efficiencies of major electric generators. In this section we will concentrate on how chemical potential and intrinsic electrical properties of materials can be used to generate smaller, but important, amounts of electricity.



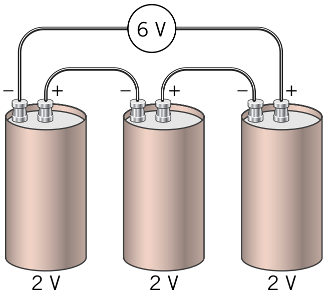
The oldest known electric battery in existence, discovered in 1938 in Baghdad, Iraq, consists of a copper tube surrounding an iron rod. If filled with an acidic liquid such as vinegar, the cell could produce a small electric current. *(Smith College Museum of Ancient Inventions)*

Batteries

One of the most familiar uses of galvanic cells, popularly called *batteries*, is the generation of portable electrical energy.[7] These devices are classified as either **primary cells** (cells not designed to be recharged; they are discarded after their energy is depleted) or **secondary cells** (cells designed for repeated use; they are able to be recharged).

Lead Storage Batteries

The common **lead storage battery** used to start an automobile is composed of a number of secondary cells, each having a potential of about 2 V, that are connected in series so that their voltages are additive. Most automobile batteries contain six such cells and give about 12 V, but 6, 24, and 32 V batteries are also available.



If three 2 volt cells are connected in series, their voltages are additive to provide a total of 6 volts. In today's autos, 12 volt batteries containing six cells are the norm.

A typical lead storage battery is illustrated in Figure 20.10. The anode of each cell is composed of a set of lead plates, the cathode consists of another set of plates that hold a coating of PbO_2, and the electrolyte is sulfuric acid. When the battery is discharging, the electrode reactions are

$$\mathrm{PbO_2}(s) + 3\mathrm{H}^+(aq) + \mathrm{HSO_4}^-(aq) + 2e^- \longrightarrow \mathrm{PbSO_4}(s) + 2\mathrm{H_2O} \qquad \text{(cathode)}$$

$$\mathrm{Pb}(s) + \mathrm{HSO_4}^-(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H}^+(aq) + 2e^- \qquad \text{(anode)}$$

The net reaction taking place in each cell is

$$\mathrm{PbO_2}(s) + \mathrm{Pb}(s) + \underbrace{2\mathrm{H}^+(aq) + 2\mathrm{HSO_4}^-(aq)}_{2\mathrm{H_2SO_4}} \longrightarrow 2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}$$

As the cell discharges, the sulfuric acid concentration decreases, which causes the density of the electrolyte to drop. The state of charge of the battery can be monitored with a **hydrometer**, which consists of a rubber bulb that is used to draw the battery fluid into a glass tube containing a float (see Figure 20.11). The depth to which the float sinks is inversely proportional to the density of the liquid—the deeper the float sinks, the lower is the density of the acid and the weaker is the charge on the battery. The narrow neck of the float is usually marked to indicate the state of charge of the battery.

The principal advantage of the lead storage battery is that the cell reactions that occur spontaneously during discharge can be reversed by the application of a voltage from an external source. In other words, the battery can be recharged by electrolysis. The reaction for battery recharge is

$$2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O} \xrightarrow{\text{electrolysis}} \mathrm{PbO_2}(s) + \mathrm{Pb}(s) + 2\mathrm{H}^+(aq) + 2\mathrm{HSO_4}^-(aq)$$

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[7] Strictly speaking, a cell is a single electrochemical unit consisting of a cathode and an anode. A battery is a collection of cells connected in series.

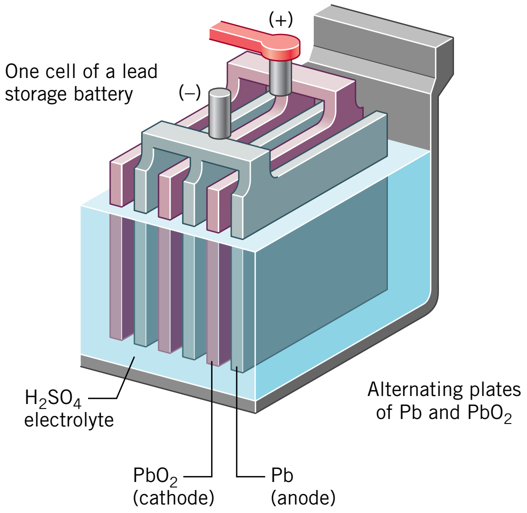

(+)
One cell of a lead storage battery
(−)
H_2SO_4 electrolyte
Alternating plates of Pb and PbO_2
PbO_2 (cathode)
Pb (anode)

Figure 20.10 | **Lead storage battery.** A 12 volt lead storage battery, such as those used in most automobiles, consists of six cells like the one shown here. Notice that the anode and cathode each consist of several plates connected together. This allows the cell to produce the large currents necessary to start a car.

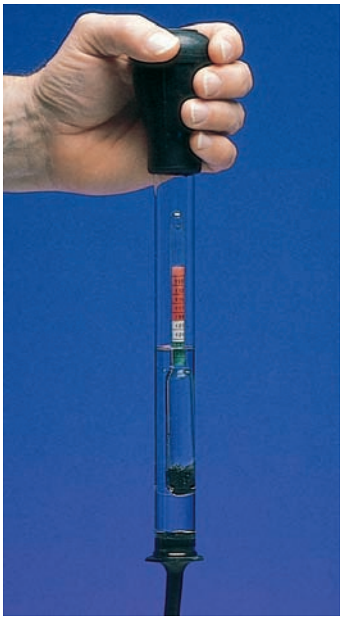


Figure 20.11 | **A battery hydrometer.** Battery acid is drawn into the glass tube. The depth to which the float sinks is inversely proportional to the concentration of the acid and, therefore, to the state of charge of the battery. *(OPC, Inc.)*

Improper recharging of lead-acid batteries can produce potentially explosive H_2 gas. Most modern lead storage batteries use a lead–calcium alloy as the anode. That reduces the need to have the individual cells vented, and the battery can be sealed, thereby preventing spillage of the corrosive electrolyte.

Zinc–Manganese Dioxide Cells

The original, relatively inexpensive 1.5 V dry cell is the **zinc–manganese dioxide cell**, or **Leclanché cell** (named after its inventor George Leclanché). It is a primary cell used to power flashlights, toys, and the like, but it is not really dry (see Figure 20.12). Its outer shell is made of zinc, which serves as the anode. The cathode—the positive terminal of the battery—consists of a carbon (graphite) rod surrounded by a moist paste of graphite powder, manganese dioxide, and ammonium chloride.

■ This is "dry" compared to the lead-acid battery, which has a significant volume of liquid sulfuric acid solution.

The anode reaction is simply the oxidation of zinc.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(anode)}$$

The cathode reaction is complex, and a mixture of products is formed. One of the major reactions is

$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O \qquad \text{(cathode)}$$

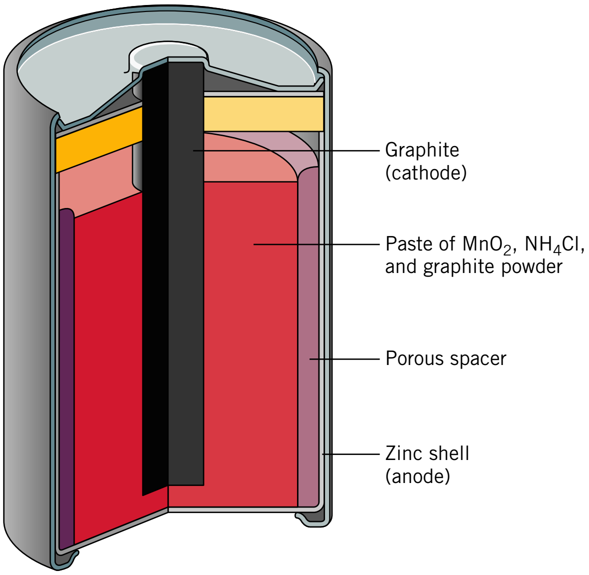


Figure 20.12 | **A cut-away view of a zinc–carbon dry cell (Leclanché cell).**

The ammonia that forms at the cathode reacts with some of the Zn^{2+} produced from the anode to form a complex ion, $Zn(NH_3)_4{}^{2+}$. Because of the complexity of the cathode half-cell reaction, no simple overall cell reaction can be written.

■ The alkaline battery is also a primary cell.

A more popular version of the Leclanché battery uses a basic, or *alkaline*, electrolyte and is called an **alkaline battery** or **alkaline dry cell.** It too uses Zn and MnO_2 as reactants, but under basic conditions (Figure 20.13). The half-cell reactions are

$$\begin{array}{lr} Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O + 2e^- & \text{(anode)} \\ 2MnO_2(s) + H_2O + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq) & \text{(cathode)} \\ \hline Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s) & \text{(net cell reaction)} \end{array}$$

and the voltage is about 1.54 V. It has a longer shelf life and is able to deliver higher currents for longer periods than the less expensive zinc–carbon cell.

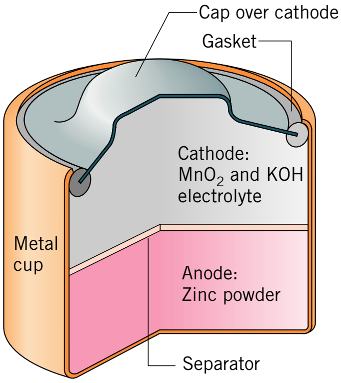


Figure 20.13 | **A simplified diagram of an alkaline dry cell.**

Nickel–Cadmium Rechargeable Batteries

The **nickel–cadmium storage cell**, or **nicad battery**, is a secondary cell that produces a potential of about 1.4 V, which is slightly lower than that of the zinc–carbon cell. The electrode reactions in the cell during discharge are

$$\begin{array}{lr} Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^- & \text{(anode)} \\ NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq) & \text{(cathode)} \\ \hline Cd(s) + NiO_2(s) + 2H_2O \longrightarrow Ni(OH)_2(s) + Cd(OH)_2(s) & \text{(net cell reaction)} \end{array}$$

The nickel–cadmium battery can be recharged, in which case the anode and cathode reactions above are reversed to remake the reactants. The battery also can be sealed to prevent leakage, which is particularly important in electronic devices.

■ If a battery can supply large amounts of energy and is contained in a small package, it will have a desirably high energy density.

Nickel–cadmium batteries work especially well in applications such as portable power tools, CD players, and even electric cars. They have a high **energy density** (available energy per unit volume), they are able to release the energy quickly, and they can be rapidly recharged.

Nickel–Metal Hydride Batteries

These secondary cells, which are often referred to as Ni–MH batteries, have been used extensively in recent years to power devices such as cell phones, camcorders, and even electric vehicles. They are similar in many ways to the alkaline nickel–cadmium cells discussed above, except for the anode reactant, which is hydrogen. This is possible because certain metal alloys [e.g., $LaNi_5$ (an alloy of lanthanum and nickel) and Mg_2Ni (an alloy of magnesium and nickel)] have the ability to absorb and hold substantial amounts of hydrogen, and the hydrogen can be made to participate in reversible electrochemical reactions. The term *metal hydride* is used to describe the hydrogen-holding alloy.

■ There are compounds of hydrogen with metals such as sodium that actually contain the *hydride ion*, H^-. The metal "hydrides" described here are not of that type.

The cathode in the Ni–MH cell is NiO(OH), a compound of nickel in the +3 oxidation state, and the electrolyte is a solution of KOH. Using the symbol MH to stand for the metal hydride, the reactions in the cell during discharge are:

$$\begin{array}{lr} MH(s) + OH^-(aq) \longrightarrow M(s) + H_2O + e^- & \text{(anode)} \\ NiO(OH)(s) + H_2O + e^- \longrightarrow Ni(OH)_2(s) + OH^-(aq) & \text{(cathode)} \end{array}$$

The overall cell reaction is

$$MH(s) + NiO(OH)(s) \longrightarrow Ni(OH)_2(s) + M(s) \qquad E^\circ_{\text{cell}} = 1.35 \text{ V}$$

When the cell is recharged, these reactions are reversed.

The principal advantage of the Ni–MH cell over the Ni–Cd cell is that it can store about 50% more energy in the same volume. This means, for example, that comparing cells of the same size and weight, a nickel–metal hydride cell can power a laptop computer or a cell phone about 50% longer than a nickel–cadmium cell.

Lithium Batteries

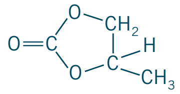
Lithium has the most negative standard reduction potential of any metal (Table 20.1), so it has a lot of appeal as an anode material. Furthermore, lithium is a very lightweight metal, so a cell employing lithium as a reactant would also be lightweight. The major problem with using lithium in a galvanic cell is that the metal reacts vigorously with water to produce hydrogen gas and lithium hydroxide.

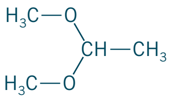
$$2\text{Li}(s) + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH}(aq) + \text{H}_2(g)$$

Therefore, to employ lithium in a galvanic cell, scientists had to find a way to avoid aqueous electrolytes. This became possible in the 1970s with the introduction of organic solvents and solvent mixtures that were able to dissolve certain lithium salts and thereby serve as electrolytes.

Today's lithium batteries fall into two categories, primary batteries that can be used once and then discarded when fully discharged, and rechargeable cells.

One of the most common nonrechargeable cells is the **lithium–manganese dioxide battery**, which accounts for about 80% of all primary lithium cells. This cell uses a solid lithium anode and a cathode made of heat-treated MnO_2. The electrolyte is a mixture of propylene carbonate and dimethoxyethane (see the structures in the margin) containing a dissolved lithium salt such as LiClO_4. The cell reactions are as follows (superscripts are the oxidation numbers of the manganese):


propylene carbonate


dimethoxyethane

$$\begin{array}{rcll}
\text{Li} & \longrightarrow & \text{Li}^+ + e^- & \text{(anode)} \\
\text{Mn}^{\text{IV}}\text{O}_2 + \text{Li}^+ + e^- & \longrightarrow & \text{Mn}^{\text{III}}\text{O}_2(\text{Li}^+) & \text{(cathode)} \\
\hline
\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 & \longrightarrow & \text{Mn}^{\text{III}}\text{O}_2(\text{Li}^+) & \text{(net cell reaction)}
\end{array}$$

This cell produces a voltage of about 3.4 V, which is more than twice that of an alkaline dry cell, and because of the light weight of the lithium, it produces more than twice as much energy for a given weight. These cells are used in applications that require a higher current drain or energy pulses (e.g., a photoflash).

Lithium Ion Cells

Rechargeable lithium batteries found in many cell phones, digital cameras, and laptop computers do not contain metallic lithium. They are called **lithium ion cells** and use lithium ions instead. In fact, the cell's operation doesn't actually involve true oxidation and reduction. Instead, it uses the transport of Li^+ ions through the electrolyte from one electrode to the other accompanied by the transport of electrons through the external circuit to maintain charge balance. Here's how it works.

It was discovered that Li^+ ions are able to slip between layers of atoms in certain crystals such as graphite[8] and LiCoO_2 (a process called **intercalation**). When the cell is constructed, it is in its "uncharged" state, with no Li^+ ions between the layers of carbon atoms in the graphite. When the cell is charged (Figure 20.14*a*), Li^+ ions leave LiCoO_2 and travel through the electrolyte to the graphite (represented below by the formula C_6).

Pronounced in-*ter*-ca-*la*-tion. Rhymes with *percolation*.

Initial charging:

$$\text{LiCoO}_2 + \text{C}_6 \longrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6$$

In these equations, the subscript *x* indicates that *some*, *but not all*, of the Li^+ ions migrate to the graphite in the charging process. Similarly, the subscript *y* represents the fraction of Li^+ ions that migrate back as electron flow is generated.

When the cell spontaneously discharges to provide electrical power (Figure 20.14*b*), Li^+ ions move back through the electrolyte to the cobalt oxide while electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode. If we represent the amount of Li^+ transferring by *y*, the discharge "reaction" is

Discharge:

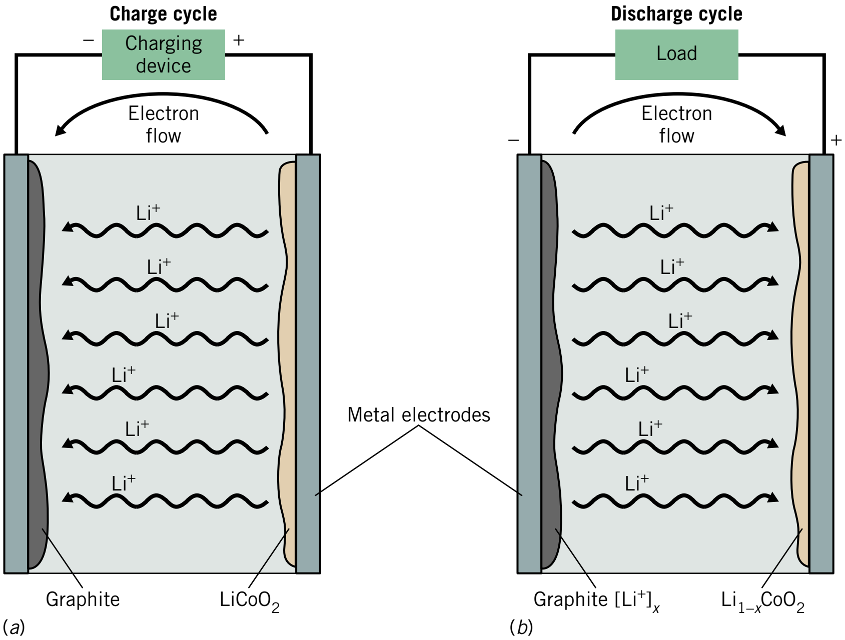
$$\text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \longrightarrow \text{Li}_{1-x+y}\text{CoO}_2 + \text{Li}_{x-y}\text{C}_6$$

Thus, the charging and discharging cycles simply sweep Li^+ ions back and forth between the two electrodes, with the electrons flowing through the external circuit to keep the charge in balance.

---

[8] Graphite is one of the forms of elemental carbon and consists of layers of joined benzene-like rings.

Figure 20.14 | **Lithium ion cell.** (*a*) During the charging cycle, an external voltage forces electrons through the external circuit and causes lithium ions to travel from the $LiCoO_2$ electrode to the graphite electrode. (*b*) During discharge, the lithium ions spontaneously migrate back to the $LiCoO_2$ electrode, and electrons flow through the external circuit to balance the charge.



Fuel Cells

The galvanic cells we've discussed until now can only produce power for a limited time because the electrode reactants are eventually depleted. Fuel cells are different; they are electrochemical cells in which the electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is required.

Figure 20.15 illustrates an early design of a hydrogen–oxygen **fuel cell**. The electrolyte, a hot (~200 °C) concentrated solution of potassium hydroxide in the center compartment, is in contact with two porous electrodes that contain a catalyst (usually platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes. At the cathode, oxygen is reduced.

$$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{(cathode)}$$

At the anode, hydrogen is oxidized to water.

$$H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O + 2e^- \qquad \text{(anode)}$$

Part of the water formed at the anode leaves as steam mixed with the circulating hydrogen gas. The net cell reaction, after making electron loss equal to electron gain, is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O \qquad \text{(net cell reaction)}$$

Hydrogen–oxygen fuel cells are an attractive alternative to gasoline-powered engines in part because they are essentially pollution-free—the only product of the reaction is harmless water. Fuel cells are also quite thermodynamically efficient, converting as much as 75% of the available energy to useful work, compared to approximately 25 to 30% for gasoline and diesel engines. Among the major obstacles are the energy costs of generating the hydrogen fuel and problems in providing storage and distribution of the highly flammable H_2.

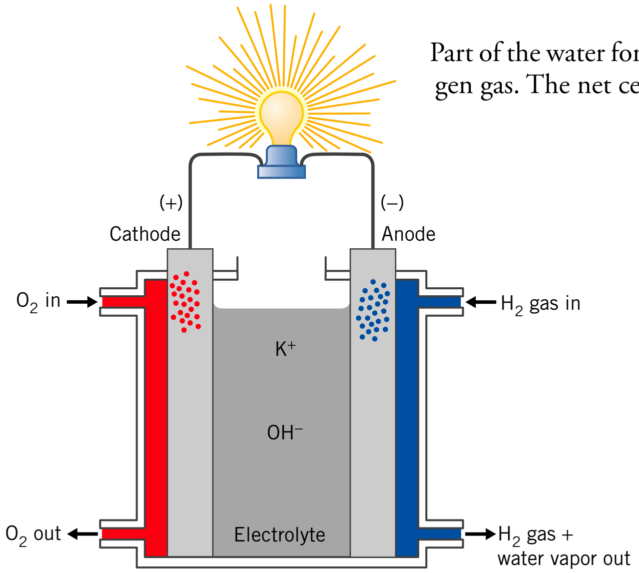


Figure 20.15 | **A hydrogen–oxygen fuel cell.**

Photovoltaic Cells

There exists a wide variety of devices where the electrical properties of materials, combined with the energy of photons, can be used to generate a flow of electrons. These devices are called *photovoltaics*. We have already laid basis of how these devices work in Chapters 8 and 10 when we discussed the photoelectric effect and solar cells.

A photovoltaic device must have a means to (a) separate an electron from a substance and (b) only allow that electron to return to its original site after moving through an external electrical circuit. In the process of traveling through the electrical circuit, the energy of that electron can be used to perform useful work.

Although modern photovoltaic devices are quite sophisticated, we can investigate a simple model to understand the basics. We start with ultrapure silicon (or germanium). These are semiconductors and are not useful until a controlled amount of impurity, in the form of phosphorous or boron, is added (this process is called doping). Referring to Chapter 10, we know that silicon should form a tetrahedral network crystal similar to diamond. If boron is added, it will replace a silicon atom in the crystal with one important difference: it can only form three bonds with the four neighboring silicon atoms. The absent bond is called a **hole** or a **positive charge carrier**. If phosphorus is added, it has five valence electrons. Four of these bond with four neighboring silicon atoms, leaving one extra electron that can move through the crystal as a **negative charge carrier**. For simplicity we call the boron doped semiconductor a *p-type* material and the phosphorus doped silicon an *n-type* semiconductor.

When n-type and p-type semiconductor materials are joined together we form a semiconductor junction that has unique properties. First, electrons from the n-type material move to the p-type material and combine with available holes. The result is a layer depleted of charge carriers, both electrons and holes. This depletion layer inhibits further flow of charge. If the negative end of a battery is connected to the n-type material, the depletion layer shrinks and electrons can flow from the n-type to the p-type material. If the battery is reversed, the depletion layer expands and electrons cannot flow in the reverse direction. This is a classic diode where electrons can flow only one way.

Now let's consider what happens if we hit these semiconductors with photons that have enough energy to excite some electrons, creating electron-hole pairs. These pairs could recombine with each other, or with other holes and electrons within the diode. That would not provide a useful flow of electrons. To be useful, another, easier, path for the electrons must be provided. We provide this pathway by adding wires (electrodes) to each side of the diode in order to connect it to an external circuit. This external circuit provides an easier route for the electrons to flow from the n-type back to the p-type material. Of course, we can add a light bulb, motor, meter, computer, or any other electric device to take advantage of this flow of electrons.

To expand our simple photocell to a useful device, we need to add a few extras as illustrated in Figure 20.16. First, we add a glass covering to protect our device from the

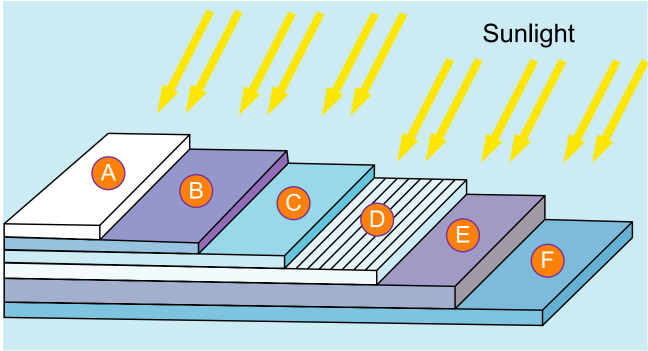


Figure 20.16 | **Diagram of the internal parts of a photovoltaic cell.** (a) Glass protective covering, (b) antireflective coating, (c) electrode mesh, (d) n-type semiconductor material, (e) p-type semiconductor material, (f) electrode. The thickness of this cell is approximately 0.3 mm, and the n-type semiconductor is approximately 0.002 mm thick.

Figure 20.17 | **Acres of photovoltaic cells can produce large amounts of energy.** *(© Fotosearch/Purestock/SuperStock)*

elements. Next, to capture all the sunlight possible, an anti-reflective coating is added, and then we have a metallic mesh cathode added to the n-type material so that light can get through. Next is the junction with the p-type semiconductor and, finally, the metal that forms the anode. Since each photovoltaic cell produces about 0.5 volt, 24 cells may be connected in series to produce a 12 volt device. Different groupings of the photo cells may be designed to improve either the voltage or current rating of the device. Figure 20.17 illustrates part of a large array of photovoltaics that could be used to power a small group of homes or stores.

20.7 | Electrolytic Cells

In our preceding discussions, we've examined how spontaneous redox reactions can be used to generate electrical energy. We now turn our attention to the opposite process, the use of electrical energy to force nonspontaneous redox reactions to occur.

When electricity is passed through a molten (melted) ionic compound or through a solution of an electrolyte, a chemical reaction occurs that we call **electrolysis.** A typical electrolysis apparatus, called an **electrolysis cell** or **electrolytic cell**, is shown in Figure 20.18. This particular cell contains molten sodium chloride. (A substance undergoing electrolysis must be molten or in solution so its ions can move freely and conduction can occur.) *Inert electrodes*—electrodes that won't react with the molten NaCl or the electrolysis products—are dipped into the cell and then connected to a source of direct current (DC) electricity.

■ To perform electrolysis, we must use direct current in which electrons move in only one direction, not in the oscillating, back and forth pattern of alternating current.

The DC source serves as an "electron pump," pulling electrons away from one electrode and pushing them through the external wiring onto the other electrode. The electrode from which electrons are removed becomes positively charged, while the other electrode becomes negatively charged. When electricity starts to flow, chemical changes begin to happen. At the positive electrode, oxidation occurs as electrons are pulled away from negatively charged chloride ions. Because of the nature of the chemical change, therefore, *the positive electrode becomes the anode*. The DC source pumps the electrons through the external electrical circuit to the negative electrode. Here reduction takes place as the electrons are forced onto positively charged sodium ions, so *the negative electrode is the cathode*.

The chemical changes that occur at the electrodes can be described by chemical equations.

$$\mathrm{Na}^+(l) + e^- \longrightarrow \mathrm{Na}(l) \qquad \text{(cathode)}$$

$$2\mathrm{Cl}^-(l) \longrightarrow \mathrm{Cl}_2(g) + 2e^- \qquad \text{(anode)}$$

As in a galvanic cell, the overall reaction that takes place in the electrolysis cell is called the *cell reaction*. To obtain it, we add the individual electrode half-reactions together,

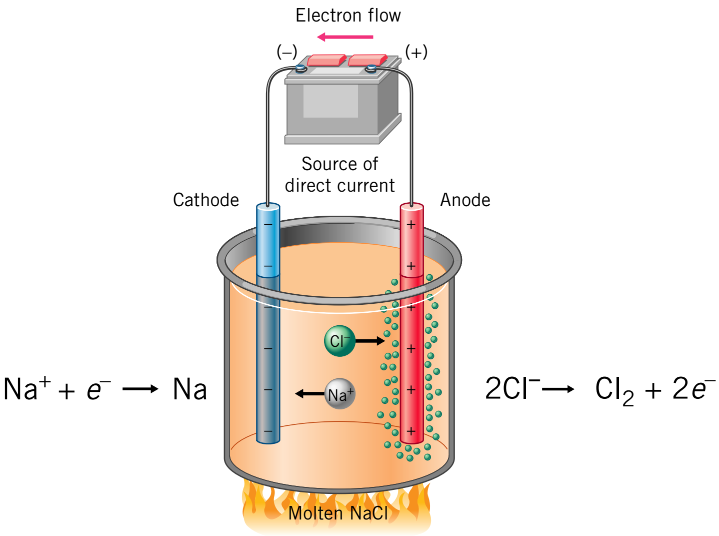


Figure 20.18 | **Electrolysis of molten sodium chloride.** In this electrolysis cell, the passage of an electric current decomposes molten sodium chloride into metallic sodium and gaseous chlorine. Unless the products are kept apart, they react on contact to re-form NaCl.

making sure that the number of electrons gained in one half-reaction equals the number lost in the other.

$$
\begin{array}{rr}
2Na^+(l) + 2e^- \longrightarrow 2Na(l) & \text{(cathode)} \\
2Cl^-(l) \longrightarrow Cl_2(g) + 2e^- & \text{(anode)} \\
\hline
2Na^+(l) + 2Cl^-(l) + \cancel{2e^-} \longrightarrow 2Na(l) + Cl_2(g) + \cancel{2e^-} & \text{(cell reaction)}
\end{array}
$$

As you know, table salt is quite stable. It doesn't normally decompose because the reverse reaction, the reaction of sodium and chlorine to form sodium chloride, is highly spontaneous. Therefore, we often write the word *electrolysis* above the arrow in the equation to show that electricity is the driving force for this otherwise nonspontaneous reaction.

$$2Na^+(l) + 2Cl^-(l) \xrightarrow{\text{electrolysis}} 2Na(l) + Cl_2(g)$$

Comparing Electrolytic and Galvanic Cells

In a galvanic cell, the spontaneous cell reaction deposits electrons on the anode and removes them from the cathode. As a result, the anode carries a slight negative charge and the cathode a slight positive charge. In most galvanic cells the reactants must be placed in separate compartments. In an *electrolysis cell*, the situation is reversed. Often the two electrodes are immersed in the same liquid. Also, the oxidation at the anode must be forced to occur, which requires that the anode be positive so it can remove electrons from the reactant at that electrode. On the other hand, the cathode must be made negative so it can force the reactant at the electrode to accept electrons.

Electrolytic Cell	**Galvanic Cell**
Cathode is negative (reduction).	Cathode is positive (reduction).
Anode is positive (oxidation).	Anode is negative (oxidation).
Anode and cathode are often in the same compartment.	Anode and cathode are usually in separate compartments.

Even though the charges on the cathode and anode differ between electrolytic cells and galvanic cells, the ions in solution always move in the same direction. In both types of cells, positive ions (cations) move toward the cathode. They are attracted there by the negative charge on the cathode in an electrolysis cell; they diffuse toward the cathode in a galvanic cell to balance the charge of negative ions left behind when ions are reduced.

■ By agreement among scientists, the names anode and cathode are assigned according to the nature of the reaction taking place at the electrode. If the reaction is oxidation, the electrode is called the anode; if it's reduction, the electrode is called the cathode.

Similarly, negative ions (anions) move toward the anode. They are attracted to the positive anode in an electrolysis cell, and they diffuse toward the anode in our galvanic cell to balance the charge of the positive ions entering the solution.

Electrolysis at the Molecular Level

The electrical conductivity of a molten salt or a solution of an electrolyte is possible only because of the reactions that take place at the surface of the electrodes. For example, when charged electrodes are dipped into molten NaCl they become surrounded by a layer of ions of the opposite charge. Let's look closely at what happens at one of the electrodes—say, the anode (Figure 20.19). Here the positive charge of the electrode attracts negative Cl^- ions, which form a coating on the electrode's surface. The charge on the anode pulls electrons from the ions, causing them to be oxidized and changing them into neutral Cl atoms that join to become Cl_2 molecules. Because the molecules are neutral, they are not held by the electrode and so move away from the electrode's surface. Their places are quickly taken by negative ions from the surrounding liquid, which tends to leave the surrounding liquid positively charged. Other negative ions from farther away move toward the anode to keep the liquid there electrically neutral. In this way, negative ions gradually migrate toward the anode. By a similar process, positive ions diffuse through the liquid toward the negatively charged cathode, where they become reduced.

■ Cations (positive ions) move toward the cathode and anions (negative ions) migrate toward the anode. This happens in both electrolytic and galvanic cells.

Electrolysis of Water in Aqueous Systems

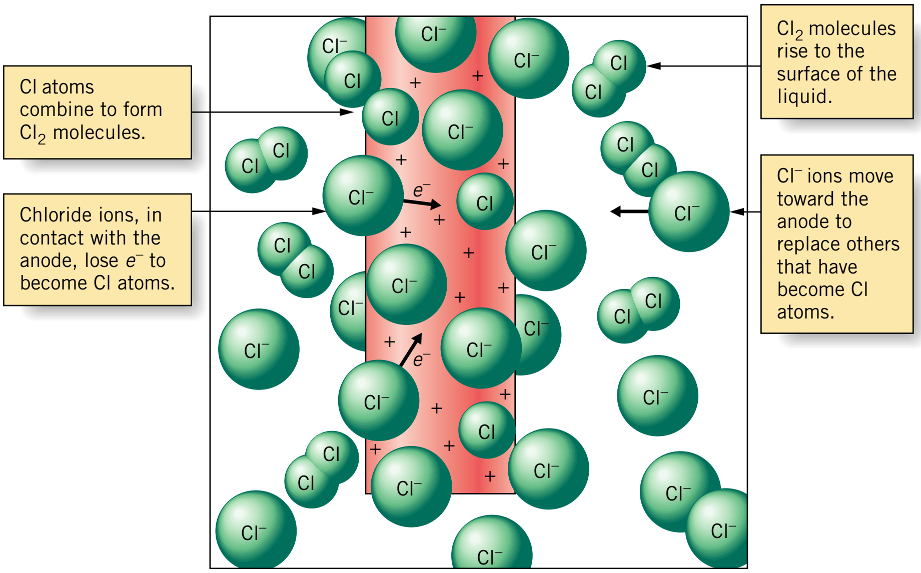
When electrolysis is carried out in an aqueous solution, the electrode reactions are more difficult to predict because at the electrodes there are competing reactions. Not only do we have to consider the possible oxidation and reduction of the solute, but also the oxidation and reduction of water. For example, consider what happens when electrolysis is performed on a solution of potassium sulfate (Figure 20.20). The products are hydrogen and oxygen. At the cathode, water is reduced, not K^+.

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad \text{(cathode)}$$

At the anode, water is oxidized, not the sulfate ion.

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(anode)}$$

Color changes of an acid–base indicator dissolved in the solution confirm that the solution becomes basic around the cathode, where OH^- is formed, and acidic around the



Cl atoms combine to form Cl_2 molecules.

Chloride ions, in contact with the anode, lose e^- to become Cl atoms.

Cl_2 molecules rise to the surface of the liquid.

Cl^- ions move toward the anode to replace others that have become Cl atoms.

Figure 20.19 | **A microscopic view of changes at the anode in the electrolysis of molten NaCl.** The positive charge of the electrode attracts a coating of Cl^- ions. At the surface of the electrode, electrons are pulled from the ions, yielding neutral Cl atoms, which combine to form Cl_2 molecules that move away from the electrode and eventually rise to the surface as a gas.

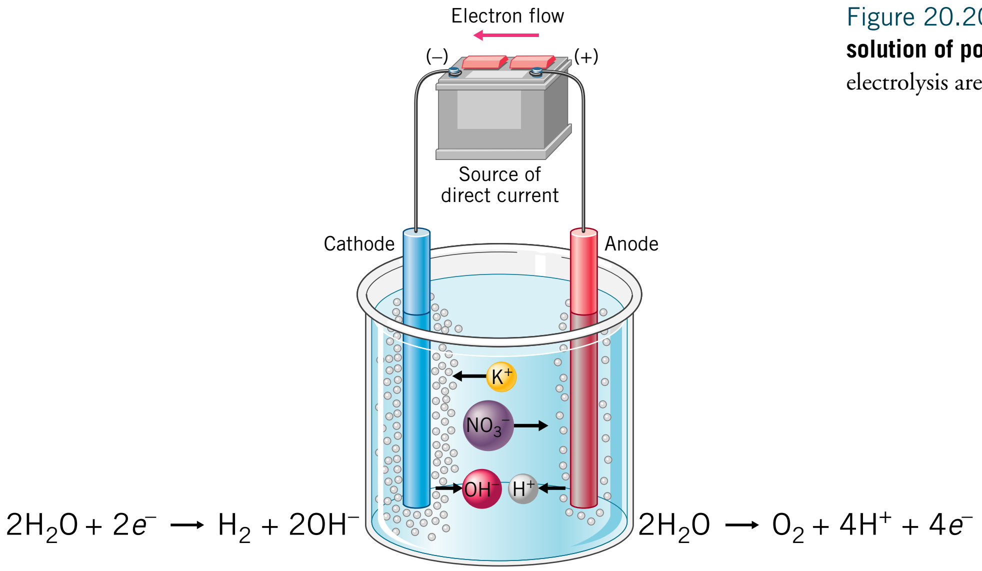

Electron flow
(–)
(+)
Source of direct current
Cathode
Anode
K^+
NO_3^-
OH^-
H^+
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Figure 20.20 | **Electrolysis of an aqueous solution of potassium sulfate.** The products of the electrolysis are the gases hydrogen and oxygen.

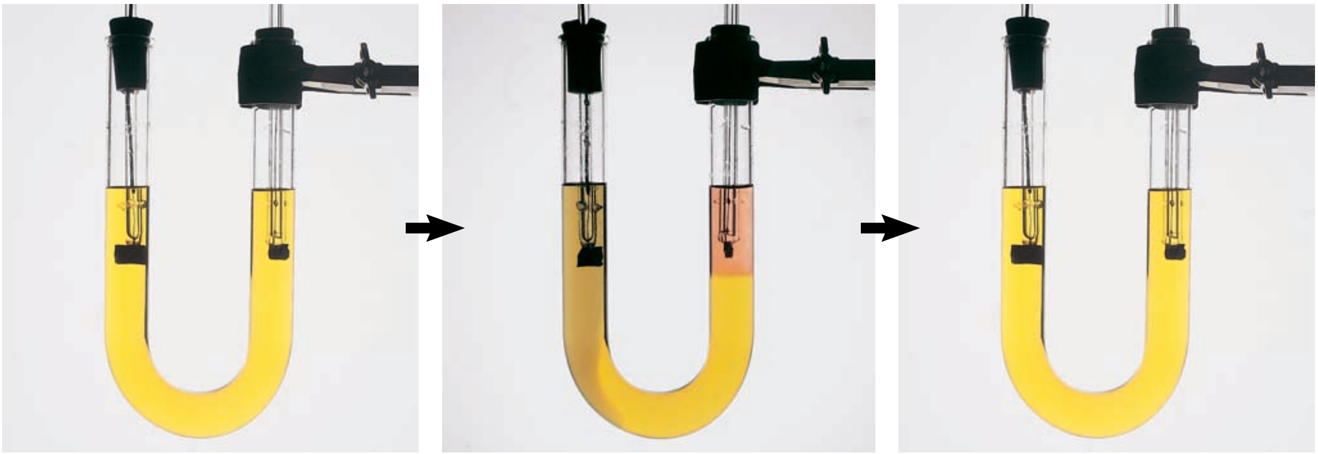
anode, where H^+ is formed (see Figure 20.21). In addition, the gases H_2 and O_2 can be separately collected.

We can understand why these redox reactions happen if we examine the standard reduction potential data from Table 20.1. For example, at the cathode we have the following competing reactions.

$$K^+(aq) + e^- \longrightarrow K(s) \qquad E^\circ_{K^+} = -2.92\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{H_2O} = -0.83\text{ V}$$

Water has a much less negative (and therefore more positive) standard reduction potential than K^+, which means H_2O is much easier to reduce than K^+. As a result, when the electrolysis is performed the more easily reduced substance is reduced and we observe H_2 being formed at the cathode.



(*a*) (*b*) (*c*)

Figure 20.21 | **Electrolysis of an aqueous solution of potassium sulfate in the presence of acid–base indicators.** (*a*) The initial yellow color indicates that the solution is neutral (neither acidic nor basic). (*b*) As the electrolysis proceeds, H^+ is produced at the anode (along with O_2) and causes the solution there to become pink. At the cathode, H_2 is evolved and OH^- ions are formed, which turns the solution around that electrode a bluish violet. (*c*) After the electrolysis is stopped and the solution is stirred, the color becomes yellow again as the H^+ and OH^- ions formed by the electrolysis neutralize each other. *(Michael Watson)*

At the anode we have the following possible oxidation half-reactions.

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$$
$$2H_2O \longrightarrow 4H^+(aq) + O_2(g) + 2e^-$$

In Table 20.1, we find them written in the opposite direction:

$$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq) \qquad E^\circ_{S_2O_8^{2-}} = +2.01\text{ V}$$
$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O \qquad E^\circ_{O_2} = +1.23\text{ V}$$

The E° values tell us that $S_2O_8^{2-}$ is much more easily reduced than O_2. But if $S_2O_8^{2-}$ is the *more easily reduced*, then the product, SO_4^{2-}, must be *the less easily oxidized*. Stated another way, *the half-reaction with the smaller standard reduction potential is more easily reversed as an oxidation*. As a result, when electrolysis is performed, water is oxidized instead of SO_4^{2-} and we observe O_2 being formed at the anode.

The overall cell reaction for the electrolysis of the K_2SO_4 solution can be obtained as before. Because the number of electrons lost has to equal the number gained, the cathode reaction must occur twice each time the anode reaction occurs once.

$$2 \times [2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)] \qquad \text{(cathode)}$$
$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(anode)}$$

After adding, we combine the coefficients for water and cancel the electrons from both sides to obtain the cell reaction.

$$6H_2O(l) \longrightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

Notice that hydrogen ions and hydroxide ions are produced in equal numbers. In Figure 20.21, we see that when the solution is stirred, they combine to form water.

$$6H_2O(l) \longrightarrow 2H_2(g) + O_2(g) + \underbrace{4H^+(aq) + 4OH^-(aq)}_{4H_2O}$$

The net change, then, is

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$

Function of Spectator Ions in Electrolysis

Although neither K^+ nor SO_4^{2-} is changed by the reaction, K_2SO_4 or some other electrolyte is needed for the electrolysis to proceed. Its function is to maintain electrical neutrality at the electrodes. At the anode, H^+ ions are formed and their charge can be balanced by mixing with SO_4^{2-} ions of the solute. Similarly, at the cathode the K^+ ions are able to mix with OH^- ions as they are formed, thereby balancing the charge and keeping the solution electrically neutral. In this way, at any moment, each small region of the solution is able to contain the same number of positive and negative charges and thereby remain neutral.

Standard Reduction Potentials and Electrolysis Products

Suppose we wish to know what products are expected in the electrolysis of an aqueous solution of copper(II) bromide, $CuBr_2$. Let's examine the possible electrode half-reactions and their respective standard reduction potentials.

At the cathode, possible reactions are the reduction of copper ion and the reduction of water. From Table 20.1,

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ_{Cu^{2+}} = +0.34\text{ V}$$
$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{H_2O} = -0.83\text{ V}$$

The much more positive reduction standard potential for Cu^{2+} tells us to anticipate that Cu^{2+} will be reduced at the cathode.

At the anode, possible reactions are the oxidation of Br^- and the oxidation of water. The half-reactions are

$$\begin{aligned} 2Br^-(aq) &\longrightarrow Br_2(aq) + 2e^- \\ 2H_2O(l) &\longrightarrow O_2(g) + 4H^+(aq) + 4e^- \end{aligned}$$

In Table 20.1, they are written as reductions with the following $E°$ values.

$$\begin{aligned} Br_2(aq) + 2e^- &\longrightarrow 2Br^-(aq) \qquad & E°_{Br_2} &= +1.07\text{ V} \\ O_2(g) + 4H^+(aq) + 4e^- &\longrightarrow 2H_2O(l) \qquad & E°_{O_2} &= +1.23\text{ V} \end{aligned}$$

The data tell us that O_2 is more easily reduced than Br_2, which means that Br^- is more easily oxidized than H_2O. Therefore, we expect that Br^- will be oxidized at the anode.

In fact, our predictions are confirmed when we perform the electrolysis. The cathode, anode, and net cell reactions are

$$\begin{array}{rcll} Cu^{2+}(aq) + 2e^- & \longrightarrow & Cu(s) & \text{(cathode)} \\ 2Br^-(aq) & \longrightarrow & Br_2(aq) + 2e^- & \text{(anode)} \\ \hline Cu^{2+}(aq) + 2Br^-(aq) & \xrightarrow{\text{electrolysis}} & Cu(s) + Br_2(aq) & \text{(net reaction)} \end{array}$$

Example 20.12
Predicting the Products in an Electrolysis Reaction

Electrolysis is planned for an aqueous solution that contains a mixture of 0.50 M $ZnSO_4$ and 0.50 M $NiSO_4$. On the basis of standard reduction potentials, what products are expected to be observed at the electrodes? What is the expected net cell reaction?

Analysis: We need to consider the competing reactions at the cathode and the anode. At the cathode, the half-reaction with the *most positive* standard reduction potential will be the one most expected to occur. At the anode, the half-reaction with the *least positive* standard reduction potential is the one that will most readily occur in the reverse, or oxidation, direction.

Assembling the Tools: Our main tool will be a table of standard reduction potentials. We can use Table 20.1, the expanded table in Appendix Table C.9, or even more extensive tables in reference works.

Solution: At the cathode, the competing reduction reactions involve the two cations and water. The reactions and their standard reduction potentials are

$$\begin{aligned} Ni^{2+}(aq) + 2e^- &\rightleftharpoons Ni(s) \qquad & E° &= -0.25\text{ V} \\ Zn^{2+}(aq) + 2e^- &\rightleftharpoons Zn(s) \qquad & E° &= -0.76\text{ V} \\ 2H_2O + 2e^- &\rightleftharpoons H_2(g) + 2OH^-(aq) \qquad & E° &= -0.83\text{ V} \end{aligned}$$

The least negative standard reduction potential is that of Ni^{2+}, so we expect this ion to be reduced at the cathode, resulting in solid nickel deposited onto the cathode.

At the anode, the competing oxidation reactions are for water and SO_4^{2-} ion. In Table 20.1, substances oxidized are found on the right side of the half-reactions. The two half-reactions having these as products are

$$\begin{aligned} S_2O_8^{2-}(aq) + 2e^- &\rightleftharpoons 2SO_4^{2-}(aq) \qquad & E° &= +2.01\text{ V} \\ O_2(g) + 4H^+(aq) + 4e^- &\rightleftharpoons 2H_2O \qquad & E° &= +1.23\text{ V} \end{aligned}$$

The half-reaction with the least positive $E°$ (the second one here) is most easily reversed as an oxidation, so we expect the oxidation half-reaction to be

$$2H_2O \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$$

At the anode, we expect O_2 to be formed.

The predicted net cell reaction is obtained by combining the two expected electrode half-reactions, making the electron loss equal to the electron gain.

$$\begin{array}{rlr} 2H_2O \longrightarrow & O_2(g) + 4H^+(aq) + 4e^- & \text{(anode)} \\ 2 \times [Ni^{2+}(aq) + 2e^- \longrightarrow & Ni(s)] & \text{(cathode)} \\ \hline 2H_2O + 2Ni^{2+}(aq) \longrightarrow & O_2(g) + 4H^+(aq) + 2Ni(s) & \text{(net cell reaction)} \end{array}$$

■ **Are the Answers Reasonable?** We can check the locations of the half-reactions in Table 20.1 to confirm our conclusions. For the reduction step, the higher up in the table a half-reaction is, the greater its tendency to occur as reduction. Among the competing half-reactions at the cathode, the one for Ni^{2+} is highest, so we expect that Ni^{2+} is the easiest to reduce and Ni(*s*) should be formed at the cathode.

For the oxidation step, the lower down in the table a half-reaction is, the easier it is to reverse and cause to occur as oxidation. On this basis, the oxidation of water is easier than the oxidation of SO_4^{2-}, so we expect H_2O to be oxidized and O_2 to be formed at the anode.

Of course, we could also test our prediction by carrying out the electrolysis experimentally.

Practice Exercises

20.23 | In the electrolysis of an aqueous solution containing Fe^{2+} and I^-, what product do we expect at the anode? (*Hint*: Write the three oxidation half-reactions possible at the anode for Fe^{2+}, I^-, and H_2O.)

20.24 | In the electrolysis of an aqueous solution containing both Cd^{2+} and Sn^{2+}, what product do we expect at the cathode?

Sometimes Predictions Fail

Although we can use standard reduction potentials to predict electrolysis reactions most of the time, there are occasions when standard reduction potentials do not successfully predict electrolysis products. Sometimes concentrations, far from standard conditions, will change the sign of the cell potential. The formation of complex ions can also interfere and produce unexpected results. And sometimes the electrodes themselves are the culprits. For example, in the electrolysis of aqueous NaCl using inert platinum electrodes, we find experimentally that Cl_2 is formed at the anode. Is this what we would have expected? Let's examine the standard reduction potentials of O_2 and Cl_2 to find out.

$$\begin{array}{rlr} Cl_2(g) + 2e^- \rightleftharpoons & 2Cl^-(aq) & E° = +1.36\text{ V} \\ O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons & 2H_2O & E° = +1.23\text{ V} \end{array}$$

Because of its less-positive standard reduction potential, we would expect the oxygen half-reaction to be the easier to reverse (with water being oxidized to O_2). Thus, standard reduction potentials predict that O_2 should be formed, but experiment shows that Cl_2 is produced. The nature of the electrode surface and how it interacts with oxygen is part of the answer. Further explanation for why this happens is beyond the scope of this text, but the unexpected result does teach us that we must be cautious in predicting products in electrolysis reactions solely on the basis of standard reduction potentials.

20.8 | Electrolysis Stoichiometry

In about 1833, Michael Faraday discovered that the amount of chemical change that occurs during electrolysis is directly proportional to the amount of electrical charge that is passed through an electrolysis cell. For example, the reduction of copper ion at a cathode is given by the equation

$$\mathrm{Cu^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s)$$

The equation tells us that to deposit one mole of metallic copper requires two moles of electrons. Thus, the half-reaction for an oxidation or reduction relates the amount of chemical substance consumed or produced to the amount of electrons that the electric current must supply. To use this information, however, we must be able to relate it to electrical measurements that can be made in the laboratory.

The SI unit of electric current is the **ampere (A)** and the SI unit of charge is the *coulomb* (C). A coulomb is the amount of charge that passes by a given point in a wire when an electric current of one ampere flows for one second. This means that coulombs are the product of amperes of current multiplied by seconds. Thus

$$1 \text{ coulomb} = 1 \text{ ampere} \times 1 \text{ second}$$

$$1\ \mathrm{C} = 1\ \mathrm{A\ s} \tag{20.9}$$

For example, if a current of 4 A flows through a wire for 10 s, 40 C pass by a given point in the wire.

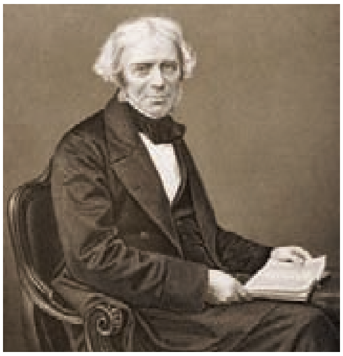
$$\begin{aligned}(4\ \mathrm{A}) \times (10\ \mathrm{s}) &= 40\ \mathrm{A\ s}\\ &= 40\ \mathrm{C}\end{aligned}$$

As we noted previously, it has been determined that 1 mol of electron carries a charge of 9.65×10^4 C, which, in honor of Michael Faraday, is often called the Faraday constant, $\mathscr{F}$.

$$1 \text{ mol } e^- \Leftrightarrow 9.65 \times 10^4\ \mathrm{C} \quad \left(\begin{array}{c}\text{to three}\\ \text{significant figures}\end{array}\right)$$

$$1\ \mathscr{F} = 9.65 \times 10^4\ \mathrm{C/mol}\ e^-$$

Now we have a way to relate laboratory measurements to the amount of chemical change that occurs during an electrolysis. Measuring the current in amperes and the time in seconds allows us to calculate the charge sent through the system in coulombs. From this we can get the amount of electrons (in moles), which we can then use to calculate the amount of chemical change produced. The following examples demonstrate the principles involved for electrolysis, but similar calculations also apply to reactions in galvanic cells. Figure 20.22 illustrates how this fits in with our previous stoichiometric calculations. We used similar pathways in Figures 4.6 and 5.27.



Michael Faraday (1791–1867), a British scientist and both a chemist and a physicist, made key discoveries leading to electric motors, generators, and transformers. *(© Classic Image/Alamy)*

TOOLS

Coulombs are related to current in amperes and time in seconds.

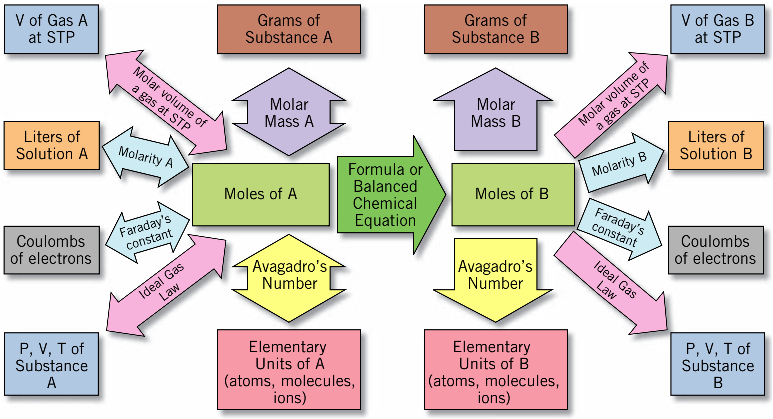

V of Gas A at STP
Grams of Substance A
Grams of Substance B
V of Gas B at STP
Molar volume of a gas at STP
Molar Mass A
Molar Mass B
Molar volume of a gas at STP
Liters of Solution A
Molarity A
Liters of Solution B
Molarity B
Moles of A
Formula or Balanced Chemical Equation
Moles of B
Faraday's constant
Faraday's constant
Coulombs of electrons
Coulombs of electrons
Ideal Gas Law
Avagadro's Number
Avagadro's Number
Ideal Gas Law
P, V, T of Substance A
Elementary Units of A (atoms, molecules, ions)
Elementary Units of B (atoms, molecules, ions)
P, V, T of Substance B

Figure 20.22 | Flowchart including electrolysis stoichiometry.

Example 20.13
Calculations Related to Electrolysis

How many grams of copper are deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through a solution of $CuSO_4$ for a period of 20.0 min?

Analysis: The wording of this question suggests that our solution will be related to a stoichiometry type of calculation in which we will convert the time and electric current to grams of copper.

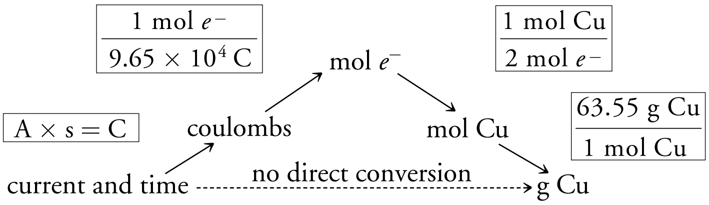
Assembling the Tools: Figure 20.22 helps us assemble the needed tools. Equation 20.9 is our tool for determining the coulombs of electrons used. Faraday's constant is used as a conversion factor to determine the moles of electrons. Next, the balanced half-reaction serves as our tool for relating moles of electrons to moles of Cu. The ion being reduced is Cu^{2+}, so the half-reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Therefore,

$$1 \text{ mol Cu} \Leftrightarrow 2 \text{ mol } e^-$$

Finally, we convert the moles of Cu to mass of Cu using the relationships from Chapter 4. Here's a diagram of the path to the solution.


$\frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}}$
$\frac{1 \text{ mol Cu}}{2 \text{ mol } e^-}$
mol e^-
$A \times s = C$
coulombs
mol Cu
$\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}}$
current and time
no direct conversion
g Cu

Since the calculation will be done stepwise we will keep an extra significant figure, that will be rounded at the end.

Solution: First we convert minutes to seconds

$$20.0 \text{ min} = 1.20 \times 10^3 \text{ s}$$

■ $20.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 1.20 \times 10^3 \text{ s}$

Then we multiply the current by the time to obtain the number of coulombs (1 A s = 1 C).

$$\begin{aligned}(1.20 \times 10^3 \text{ s}) \times (2.00 \text{ A}) &= 2.40 \times 10^3 \text{ A s} \\ &= 2.40 \times 10^3 \text{ C}\end{aligned}$$

Because 1 mol $e^- \Leftrightarrow 9.65 \times 10^4$ C,

$$2.40 \times 10^3 \ \cancel{\text{C}} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \ \cancel{\text{C}}} = 0.02487 \text{ mol } e^-$$

Next, we use the relationship between mol e^- and mol Cu from the balanced half-reaction along with the atomic mass of copper.

$$0.02487 \ \cancel{\text{mol } e^-} \times \left(\frac{1 \ \cancel{\text{mol Cu}}}{2 \ \cancel{\text{mol } e^-}}\right) \times \left(\frac{63.55 \text{ g Cu}}{1 \ \cancel{\text{mol Cu}}}\right) = 0.7903 \text{ g Cu}$$

With proper rounding the electrolysis will deposit 0.790 g of copper on the cathode.

We could have combined all these steps in a single calculation by stringing together the various conversion factors and using the factor-label method to cancel units. In the equation below we are writing 9.65×10^4 C as the equivalent 9.65×10^4 A s.

$$2.00 \ \cancel{\text{A}} \times 20.0 \ \cancel{\text{min}} \times \frac{60 \ \cancel{\text{s}}}{1 \ \cancel{\text{min}}} \times \frac{1 \ \cancel{\text{mol } e^-}}{9.65 \times 10^4 \ \cancel{\text{A}} \ \cancel{\text{s}}} \times \frac{1 \ \cancel{\text{mol Cu}}}{2 \ \cancel{\text{mol } e^-}} \times \frac{63.55 \text{ g Cu}}{1 \ \cancel{\text{mol Cu}}} = 0.790 \text{ g Cu}$$

Is the Answer Reasonable? As before, we round all numbers to one significant figure to estimate the answer. To be sure the problem is set up correctly, cancel the units as we did in the solution.

$$\text{g Cu} = 2\ \text{A} \times 20\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{1\ \text{mol}\ e^-}{10 \times 10^4\ \text{A s}} \times \frac{1\ \text{mol Cu}}{2\ \text{mol}\ e^-} \times \frac{60\ \text{g Cu}}{1\ \text{mol Cu}}$$

$$= \frac{40 \times 3600}{200{,}000} = \frac{40 \times 0.36}{20} = 0.72\ \text{g Cu}$$

This is very close to our answer, and we are even more confident that the calculation was correct when we supply the cancellation of units to our estimate.

Example 20.14
Calculations Related to Electrolysis

Electrolysis provides a useful way to deposit a thin metallic coating on an electrically conducting surface. This technique is called electroplating. How much time would it take, in minutes, to deposit 0.500 g of metallic nickel on a metal object using a current of 3.00 A? The nickel is reduced from the +2 oxidation state.

Analysis: This problem is essentially the reverse of Example 20.13. We will perform a stoichiometric calculation starting with the given mass of nickel and ending with the coulombs needed.

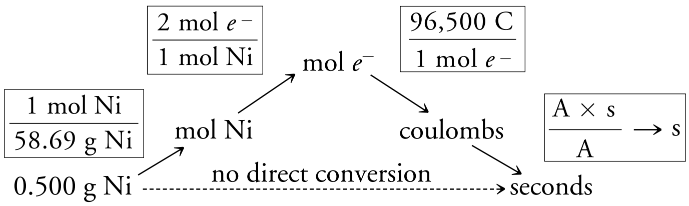
Assembling the Tools: We should be very familiar with converting mass to moles; the next step requires a balanced chemical equation. Because the nickel is reduced to the free metal from the +2 state, we can write

$$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}(s)$$

This gives the relationship

$$1\ \text{mol Ni} \Leftrightarrow 2\ \text{mol}\ e^-$$

which allows us to calculate the number of moles of electrons required. This, in turn, is used with the tool for the Faraday constant to determine the number of coulombs required. Equation 20.9 tells us that this is the product of amperes and seconds; so we can calculate the time needed to deposit the metal. The diagram below isolates our sequence of steps that can also be deduced from Figure 20.22.



Solution: First, we calculate the number of moles of electrons required (keeping at least one extra significant figure).

In stepwise calculations we usually carry one or more extra significant figures to minimize rounding errors.

$$0.500\ \cancel{\text{g Ni}} \times \left(\frac{1\ \cancel{\text{mol Ni}}}{58.69\ \cancel{\text{g Ni}}}\right) \times \left(\frac{2\ \text{mol}\ e^-}{1\ \cancel{\text{mol Ni}}}\right) = 0.01704\ \text{mol}\ e^-$$

Then we calculate the number of coulombs needed.

$$0.01704\ \cancel{\text{mol}\ e^-} \times \left(\frac{9.65 \times 10^4\ \text{C}}{1\ \cancel{\text{mol}\ e^-}}\right) = 1.644 \times 10^3\ \text{C}$$

$$= 1.644 \times 10^3\ \text{A s}$$

■ Once we've calculated the number of coulombs required, we can calculate the time required if we know the current, or the current needed to perform the electrolysis in a given time.

This tells us that the product of current multiplied by time equals 1.644×10^3 A s. The current is 3.00 A. Dividing 1.644×10^3 A s by 3.00 A gives the time required in seconds, which we then convert to minutes.

$$\left(\frac{1.644 \times 10^3\ \cancel{\text{A}}\ \cancel{\text{s}}}{3.00\ \cancel{\text{A}}}\right) \times \left(\frac{1\ \text{min}}{60\ \cancel{\text{s}}}\right) = 9.133\ \text{min}$$

Properly rounded, this becomes 9.13 min. We could also have combined these calculations in a single string of conversion factors.

$$0.500\ \cancel{\text{g Ni}} \times \frac{1\ \cancel{\text{mol Ni}}}{58.69\ \cancel{\text{g Ni}}} \times \frac{2\ \cancel{\text{mol}\ e^-}}{1\ \cancel{\text{mol Ni}}} \times \frac{9.65 \times 10^4\ \cancel{\text{A}}\ \cancel{\text{s}}}{1\ \cancel{\text{mol}\ e^-}} \times \frac{1}{3.00\ \cancel{\text{A}}} \times \frac{1\ \text{min}}{60\ \cancel{\text{s}}} = 9.13\ \text{min}$$

■ **Is the Answer Reasonable?** As in the preceding example, let's round all numbers to one digit as

$$\begin{aligned} \text{min} &= 0.5\ \text{g Ni} \times \frac{1\ \text{mol Ni}}{60\ \text{g Ni}} \times \frac{2\ \text{mol}\ e^-}{1\ \text{mol Ni}} \times \frac{10 \times 10^4\ \text{A s}}{1\ \text{mol}\ e^-} \times \frac{1}{3\ \text{A}} \times \frac{1\ \text{min}}{60\ \text{s}} \\ &= \frac{100{,}000}{3{,}600 \times 3} = \frac{100{,}000}{10{,}000} = 10\ \text{min} \end{aligned}$$

This result, along with the proper cancellation of units, indicates that our setup and calculations were correct.

Practice Exercises

20.25 | How many moles of hydroxide ion will be produced at the cathode during the electrolysis of water with a current of 4.00 A for a period of 3.00 minutes? The cathode reaction is

$$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$$

(*Hint*: The stepwise diagram in Example 20.14 will be helpful.)

20.26 | How many minutes will it take for a current of 10.0 A to deposit 3.00 g of gold from a solution of $AuCl_3$?

20.27 | What current must be supplied to deposit 3.00 g of gold from a solution of $AuCl_3$ in 20.0 min?

20.28 | Suppose the solutions in the galvanic cell depicted in Figure 20.2 (page 920) have a volume of 125 mL and suppose the cell is operated for a period of 1.25 hr with a constant current of 0.100 A flowing through the external circuit. By how much will the concentration of the copper ion increase during this time period?

20.9 | Practical Applications of Electrolysis

Electrochemistry has many applications both in science and in our everyday lives. In this limited space, we can only touch on some of the more common and important examples of the industrial uses of electrolysis.

Industrial Applications

Besides being a useful tool in the chemistry laboratory, electrolysis has many important industrial applications. In this section we will briefly examine the chemistry of electroplating and the production of some of our most common chemicals.

Electroplating

Electroplating, which was mentioned in Examples 20.13 and 20.14, is a procedure in which electrolysis is used to apply a thin (generally 0.03 to 0.05 mm thick) ornamental or protective coating of one metal over another. It is a common technique for improving the appearance and durability of metal objects. For instance, a thin, shiny coating of metallic chromium is applied over steel objects to make them attractive and to prevent rusting.

The exact composition of the electroplating bath varies, depending on the metal to be deposited, and it can affect the appearance and durability of the finished surface. For example, silver deposited from a solution of silver nitrate ($AgNO_3$) does not stick to other metal surfaces very well. However, if it is deposited from a solution of silver cyanide containing $Ag(CN)_2^-$, the coating adheres well and is bright and shiny. Other metals that are electroplated from a cyanide bath are gold and cadmium. Nickel, which can also be applied as a protective coating, is plated from a nickel sulfate solution, and chromium is plated from a chromic acid (H_2CrO_4) solution.

This motorcycle sparkles with chrome plating that was deposited by electrolysis. The shiny, hard coating of chromium is both decorative and a barrier to corrosion. *(Syracuse Newspapers/ The Image Works)*

Production of Aluminum

Aluminum is a useful but highly reactive metal. It is so difficult to reduce that ordinary metallurgical methods for obtaining it do not work. Early efforts to produce aluminum by electrolysis failed because its anhydrous halide salts (those with no water of hydration) are difficult to prepare and are volatile, tending to evaporate rather than melt. On the other hand, its oxide, Al_2O_3, has such a high melting point (over 2000 °C) that no practical method of melting it could be found.

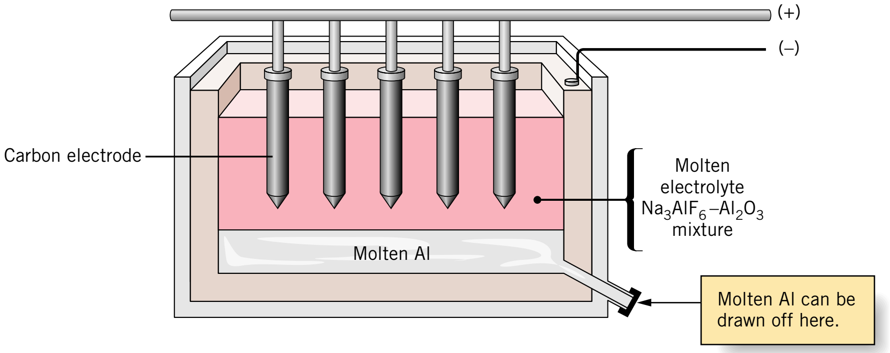
■ Aluminum is used today as a structural metal, in alloys, and in such products as aluminum foil, electrical wire, window frames, and kitchen pots and pans.

In 1886, Charles M. Hall discovered that Al_2O_3 dissolves in the molten form of a mineral called cryolite, Na_3AlF_6, to give a conducting mixture with a relatively low melting point from which aluminum could be produced electrolytically. The process was also discovered by Paul Héroult in France at nearly the same time, and today this method for producing aluminum is usually called the **Hall–Héroult process** (see Figure 20.23). Purified aluminum oxide, which is obtained from an ore called *bauxite,* is dissolved in molten cryolite in which the oxide dissociates to give Al^{3+} and O^{2-} ions. At the cathode, aluminum ions are reduced to produce the free metal, which forms as a layer of molten aluminum below the less dense solvent. At the carbon anodes, the oxide ion is oxidized to give free O_2.

$$\begin{array}{rcll} Al^{3+} + 3e^- & \longrightarrow & Al(l) & \text{(cathode)} \\ 2O^{2-} & \longrightarrow & O_2(g) + 4e^- & \text{(anode)} \\ \hline 4Al^{3+} + 6O^{2-} & \longrightarrow & 4Al(l) + 3O_2(g) & \text{(cell reaction)} \end{array}$$

The oxygen formed at the anode attacks the carbon electrodes (producing CO_2), so the electrodes must be replaced frequently.

The production of aluminum consumes enormous amounts of electrical energy and is therefore very costly, not only in terms of dollars but also in terms of energy resources. For this reason, recycling of aluminum has a high priority as we seek to minimize our use of energy.



Molten Al can be drawn off here.

Figure 20.23 | **Production of aluminum by electrolysis.** In the apparatus used to produce aluminum electrolytically by the Hall–Héroult process, Al_2O_3 is dissolved in molten cryolite, Na_3AlF_6. The Al^{3+} is reduced to metallic Al, and O^{2-} is oxidized to O_2, which reacts with the carbon anodes to give CO_2. Periodically, molten aluminum is drawn off at the bottom of the cell and additional Al_2O_3 is added to the cryolite. The carbon anodes also must be replaced from time to time as they are consumed by their reaction with O_2.

Production of Sodium

Sodium is prepared by the electrolysis of molten sodium chloride (see Section 20.6). The metallic sodium and the chlorine gas that form must be kept apart or they will react violently and re-form NaCl. A specialized apparatus called a **Downs cell** accomplishes this separation.

Both sodium and chlorine are commercially important. Chlorine is used largely to manufacture plastics such as polyvinyl chloride (PVC), many solvents, and industrial chemicals. A small percentage of the annual chlorine production is used to chlorinate drinking water.

Sodium has been used in the manufacture of tetraethyl lead, an octane booster for gasoline that has been phased out in the United States but is still used in many other countries. Sodium is also used in the production of energy-efficient sodium vapor lamps, which give street lights and other commercial lighting a bright yellow-orange color.

■ PVC is used to make a large variety of products, from raincoats to wire insulation to pipes and conduits for water and sanitary systems. In the United States, the annual demand for PVC plastics is about 15 billion pounds.

Copper refining. Copper cathodes, 99.96% pure, are pulled from the electrolytic refining tanks at Kennecott's Utah copper refinery. It takes about 28 days for the impure copper anodes to dissolve and deposit the pure metal on the cathodes. *(Courtesy James Brady)*

Refining Copper

When copper is first obtained from its ore, it is about 99% pure. The impurities—mostly silver, gold, platinum, iron, and zinc—decrease the electrical conductivity of the copper enough that even 99% pure copper must be further refined before it can be used in electrical wire.

The impure copper is used as the anode in an electrolysis cell that contains a solution of copper sulfate and sulfuric acid as the electrolyte (see Figure 20.24). The cathode is a thin sheet of very pure copper. When the cell is operated at the correct voltage, only copper and impurities more easily oxidized than copper (iron and zinc) dissolve at the anode. The less active metals simply fall off the electrode and settle to the bottom of the container. At the cathode, copper ions are reduced, but the zinc ions and iron ions remain in solution because they are more difficult to reduce than copper. Gradually, the impure copper anode dissolves and the copper cathode, about 99.96% pure, grows larger. The accumulating sludge—called anode mud—is removed periodically, and the value of the silver, gold, and platinum recovered from it virtually pays for the entire refining operation.

■ Copper refining provides one-fourth of the silver and one-eighth of the gold produced annually in the United States.

Electrolysis of Brine

One of the most important commercial electrolysis reactions is the electrolysis of concentrated aqueous sodium chloride solutions called **brine**. Water is much more easily reduced than sodium ions, so H_2 forms at the cathode.

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad \text{(cathode)}$$

As we noted earlier, even though water is more easily oxidized than chloride ions, complicating factors at the electrode surface actually allow chloride ions to be oxidized more readily than water. At the anode, therefore, we observe the formation of Cl_2.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad \text{(anode)}$$

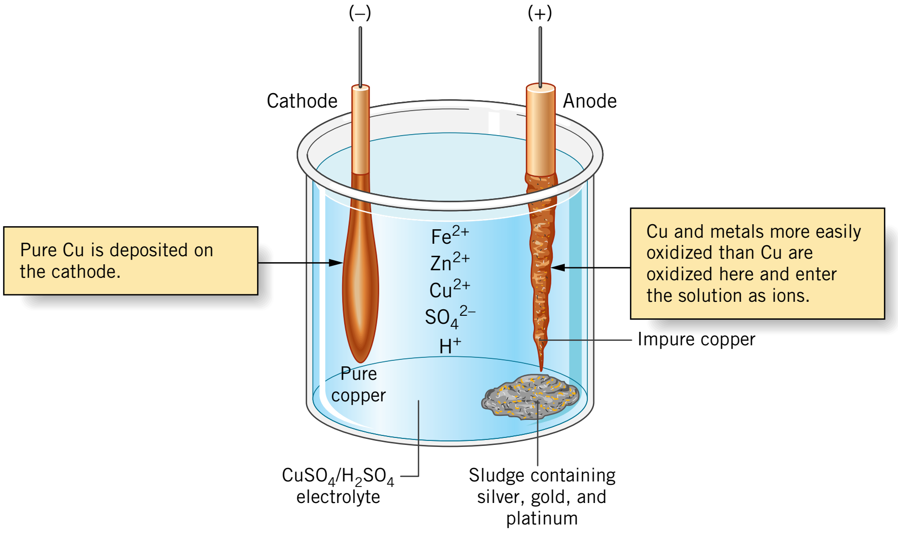

(–)
(+)
Cathode
Anode
Pure Cu is deposited on the cathode.
Fe^{2+}
Zn^{2+}
Cu^{2+}
SO_4^{2-}
H^+
Cu and metals more easily oxidized than Cu are oxidized here and enter the solution as ions.
Impure copper
Pure copper
$CuSO_4/H_2SO_4$ electrolyte
Sludge containing silver, gold, and platinum

Figure 20.24 | **Purification of copper by electrolysis.** Impure copper anodes dissolve and pure copper is deposited on the cathodes. Metals less easily oxidized than copper settle to the bottom of the apparatus as "anode mud," while metals less easily reduced than copper remain in solution.

The net cell reaction is therefore

$$2Cl^-(aq) + 2H_2O(l) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$$

If we include the sodium ion, already in the solution as a spectator ion and not involved in the electrolysis directly, we can see why this is such an important reaction.

$$\underbrace{2Na^+(aq) + 2Cl^-(aq)}_{2NaCl(aq)} + 2H_2O \xrightarrow{\text{electrolysis}} H_2(g) + Cl_2(g) + \underbrace{2Na^+(aq) + 2OH^-(aq)}_{2NaOH(aq)}$$

Thus, the electrolysis converts inexpensive salt to valuable chemicals: H_2, Cl_2, and NaOH. The hydrogen is used to make other chemicals, including hydrogenated vegetable oils. The chlorine is used for the purposes mentioned earlier. Among the uses of sodium hydroxide, one of industry's most important bases, are the manufacture of soap and paper, the neutralization of acids in industrial reactions, and the purification of aluminum ores.

■ Sodium hydroxide is commonly known as *lye* or *caustic soda.*

In the industrial electrolysis of brine, it is necessary to capture the H_2 and Cl_2 separately to prevent them from mixing and reacting (explosively). Second, the NaOH from the reaction is contaminated with unreacted NaCl. Third, if Cl_2 is left in the presence of NaOH, the solution becomes contaminated by hypochlorite ions (OCl^-), which form when Cl_2 reacts with OH^-.

$$Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + OCl^-(aq) + H_2O$$

In one manufacturing operation, however, the Cl_2 is not removed as it forms, and its reaction with hydroxide ion is used to manufacture aqueous sodium hypochlorite. For this purpose, the solution is stirred vigorously during the electrolysis so that very little Cl_2 escapes. As a result, a stirred solution of NaCl gradually changes during electrolysis to a solution of NaOCl, a dilute, 5% solution of which is sold as liquid laundry bleach (e.g., Clorox).

Most of the pure NaOH manufactured today is made in an apparatus called a **diaphragm cell**. The design varies somewhat, but Figure 20.25 illustrates its basic features. The cell consists of an iron wire mesh cathode that encloses a porous asbestos shell—

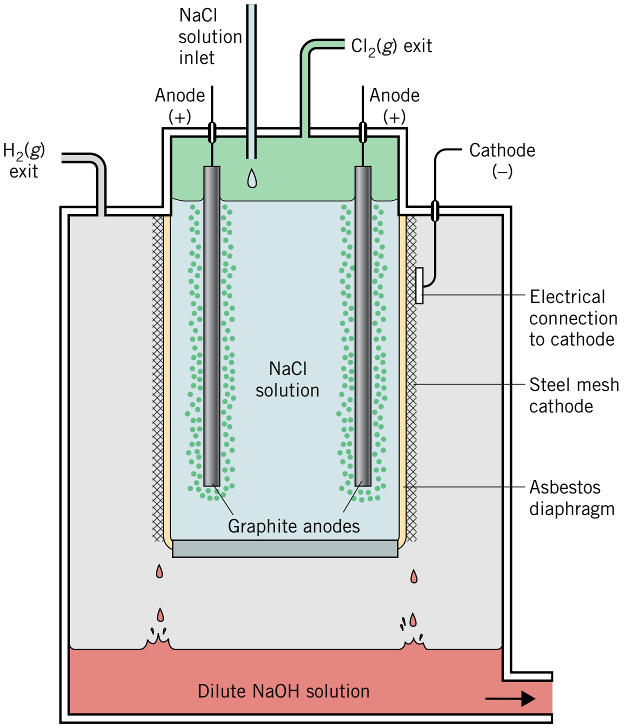


Figure 20.25 | **A diaphragm cell used in the commercial production of NaOH by the electrolysis of aqueous NaCl.** This is a cross section of a cylindrical cell in which the NaCl solution is surrounded by an asbestos diaphragm supported by a steel mesh cathode. *(From J. E. Brady and G. E. Humiston,* General Chemistry: Principles and Structure, *5th ed. Copyright © 1986, John Wiley & Sons, New York. Used by permission.)*

the diaphragm. The NaCl solution is added to the top of the cell and seeps slowly through the diaphragm. When it contacts the iron cathode, hydrogen is evolved and is pumped out of the surrounding space. The solution, now containing dilute NaOH, drips off the cell into the reservoir below. Meanwhile, within the cell, chlorine is generated at the anodes. Because there is no OH^- near the anodes, the Cl_2 can't react to form the OCl^- ion and simply bubbles out of the solution and is captured as illustrated in the figure.

Summary

Galvanic Cells. A **galvanic cell** is composed of two **half-cells,** each containing an **electrode** in contact with an electrolyte reactant. A spontaneous redox reaction is thus divided into separate oxidation and reduction half-reactions, with the electron transfer occurring through an external electrical circuit. Reduction occurs at the **cathode;** oxidation occurs at the **anode.** In a galvanic cell, the cathode is positively charged and the anode is negatively charged. The half-cells must be connected electrolytically by a **salt bridge** to complete the electrical circuit, which permits electrical neutrality to be maintained by allowing cations to move toward the cathode and anions toward the anode.

The **potential** (expressed in volts) produced by a cell is equal to the **standard cell potential** when all ion concentrations are 1.00 *M* and the partial pressures of any gases involved equal 1.00 atm and the temperature is 25.0 °C. The **standard cell potential** is the difference between the **standard reduction potentials** of the half-cells. In the spontaneous reaction, the half-cell with the higher standard reduction potential undergoes reduction and forces the other to undergo oxidation. The standard reduction potentials of isolated half-cells can't be measured, but values are assigned by choosing the **hydrogen electrode** as a reference electrode; its standard reduction potential is assigned a value of exactly 0.00 V. Species more easily reduced than H^+ have positive standard reduction potentials; those less easily reduced have negative standard reduction potentials. Standard reduction potentials are used to calculate E°_{cell}. Standard reduction potentials can be used to predict whether or not a redox reaction will be spontaneous, whether or not the reaction is carried out in a galvanic cell. Often, standard reduction potentials can be used to determine the products of electrolysis reactions. Since reduction potentials under nonstandard conditions are often numerically close to standard reduction potentials, we can usually use standard reduction potentials to make predictions about reactions with nonstandard conditions.

Thermodynamics and Cell Potentials. The values of ΔG° and K_c for a reaction can be calculated from E°_{cell}. They all involve the **faraday,** $\mathscr{F}$, a constant equal to the number of **coulombs (C)** of charge per mole of electrons ($1\mathscr{F} = 96{,}485$ C/mol e^-). The **Nernst equation** relates the cell potential to the standard cell potential and the reaction quotient. It is used to calculate the cell potential under nonstandard conditions. If the cell potential is measured, the Nernst equation may be used to determine concentrations.

Electrolysis. In an **electrolytic cell,** a flow of electricity causes an otherwise nonspontaneous reaction to occur. A negatively charged **cathode** causes reduction of one reactant and a positively charged **anode** causes oxidation of another. Ion movement instead of electron transport occurs in the electrolyte. The electrode reactions are determined by which species is most easily reduced and which is most easily oxidized, but in aqueous solutions complex surface effects at the electrodes can alter the natural order. In the electrolysis of water, an electrolyte must be present to maintain electrical neutrality at the electrodes.

Quantitative Aspects of Electrochemical Reactions. The product of current (**amperes**) and time (seconds) gives coulombs. This relationship and the half-reactions that occur at the anode or cathode permit us to relate the amount of chemical change to measurements of current and time.

Practical Galvanic Cells. The **lead storage battery** and the **nickel–cadmium (nicad) battery** are **secondary cells** and are rechargeable. The state of charge of the lead storage battery can be tested with a **hydrometer**, which measures the density of the sulfuric acid electrolyte. The **zinc–manganese dioxide cell** (the **Leclanché cell** or common dry cell) and the common **alkaline battery** (which uses essentially the same reactions as the less expensive dry cell) are **primary cells** and are not rechargeable. The rechargeable **nickel–metal hydride** (Ni–MH) battery uses hydrogen contained in a metal alloy as its anode reactant and has a higher **energy density** than the nicad battery. Primary **lithium–manganese dioxide cells** and rechargeable **lithium ion cells** produce a large cell potential and have a very large energy density. Lithium ion cells store and release energy by transferring lithium ions between electrodes where the Li^+ are **intercalated** between layers of atoms in the electrode materials. **Fuel cells**, which have high thermodynamic efficiencies, are able to provide continuous power because they consume fuel that can be fed continuously. **Photovoltaic cells** are based on semiconductor technology where the junction between a **p-type** and an **n-type** semiconductor produces a device called a **diode** that allows electrons to flow in only one direction. Once photons separate an electron from the semiconductor material, the properties of a diode make it easier for electrons to flow through an external circuit.

Applications of Electrolysis. **Electroplating,** the production of aluminum, the **refining** of copper, and the electrolysis of molten and aqueous sodium chloride are examples of practical applications of electrolysis.

Tools for Problem Solving The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Electrode names and reactions (page 921)

Scientists have agreed to name electrodes based on the reaction that occurs. The **cathode** is the electrode at which reduction (electron gain) occurs. The **anode** is the electrode at which oxidation (electron loss) occurs.

Standard reduction potentials used to calculate E°_{cell} (page 925)

In a galvanic cell, the difference between two standard reduction potentials equals the standard cell potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$$

Standard cell potentials are always positive, and the reaction that gives us a positive standard cell potential will be a spontaneous reaction at standard state (page 934). Comparing standard reduction potentials also lets us predict the electrode reactions in electrolysis (page 956).

Faraday constant (page 936)

Besides being a constant in the equations below, the Faraday constant allows us to relate coulombs (obtained from the product of current and time) to moles of chemical change in electrochemical reactions.

$$1\mathscr{F} = 96{,}485.340 \text{ C/mol } e^-$$

Standard cell potentials are related to thermodynamic quantities

The relationship between the cell potential E_{cell} and the free energy, ΔG is: $\Delta G = -n\mathscr{F}E$ (page 937)

The relationship between the standard cell potential, E°_{cell}, and the standard free energy, ΔG° is: $\Delta G^\circ = -n\mathscr{F}E^\circ$ (page 937).

The relationship between the standard cell potential, E°_{cell}, and the equilibrium constant, K_c, is: $E^\circ_{\text{cell}} = \dfrac{RT}{n\mathscr{F}} \ln K_c$ (page 938).

Standard cell potentials are also needed to solve the Nernst equation (below) to relate concentrations of species in galvanic cells to the cell potential.

Nernst equation (page 940)

The Nernst equation lets us relate the cell potential, E_{cell}, the standard cell potential, E°_{cell}, and concentration data.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathscr{F}} \ln Q$$

We can also calculate the concentration of a species in solution from E°_{cell} and a measured value for E_{cell} (page 943).

Coulombs are related to current in amperes and time in seconds (page 959)

Coulombs, C, can be experimentally determined as the current, A, multiplied by time, t, in seconds. Combined with the faraday, the moles of electrons can be determined.

$$\text{C} = \text{A} \times t$$

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Galvanic Cells

20.1 What is a galvanic cell? What is a half-cell?

20.2 What is the function of a *salt bridge*?

20.3 In the copper–silver cell, why must the Cu^{2+} and Ag^+ solutions be kept in separate containers?

20.4 Which redox processes take place at the anode and cathode in a galvanic cell? What is the sign of the electrical charges on the anode and cathode in a galvanic cell?

20.5 In a galvanic cell, do electrons travel from anode to cathode, or from cathode to anode? Explain.

20.6 Explain how the movement of the ions relative to the electrodes is the same in both galvanic and electrolytic cells.

20.7 Aluminum will displace tin from solution according to the equation $2\mathrm{Al}(s) + 3\mathrm{Sn}^{2+}(aq) \longrightarrow 2\mathrm{Al}^{3+}(aq) + 3\mathrm{Sn}(s)$. What would be the individual half-cell reactions if this were the cell reaction for a galvanic cell? Which metal would be the anode and which the cathode?

Cell Potentials and Reduction Potentials

20.8 What is the difference between a *cell potential* and a *standard cell potential*?

20.9 How are standard reduction potentials combined to give the standard cell potential for a spontaneous reaction?

20.10 Describe the hydrogen electrode. What is the value of its standard reduction potential?

20.11 What do the positive and negative signs of reduction potentials tell us?

20.12 If $E^\circ_{\mathrm{Cu}^{2+}}$ had been chosen as the standard reference electrode and had been assigned a potential of 0.00 V, what would the reduction potential of the hydrogen electrode be relative to it?

20.13 If you set up a galvanic cell using metals not found in Table 20.1, what experimental information will tell you which is the anode and which is the cathode in the cell?

Using Standard Reduction Potentials

20.14 Compare Table 6.3 with Table 20.1. What can you say about the basis for the activity series for metals?

20.15 Make a sketch of a galvanic cell for which the cell notation is

$$\mathrm{Fe}(s)\,|\,\mathrm{Fe}^{3+}(aq)\,||\,\mathrm{Ag}^{+}(aq)\,|\,\mathrm{Ag}(s)$$

(a) Label the anode and the cathode.

(b) Indicate the charge on each electrode.

(c) Indicate the direction of electron flow in the external circuit.

(d) Write the equation for the net cell reaction.

20.16 Make a sketch of a galvanic cell in which inert platinum electrodes are used in the half-cells for the system

$$\mathrm{Pt}(s)\,|\,\mathrm{Fe}^{2+}(aq),\ \mathrm{Fe}^{3+}(aq)\,||\,\mathrm{Br}_2(aq),\ \mathrm{Br}^-(aq)\,|\,\mathrm{Pt}(s)$$

Label the diagram and indicate the composition of the electrolytes in the two cell compartments. Show the signs of the electrodes and label the anode and cathode. Write the equation for the net cell reaction.

Cell Potentials and Thermodynamics

20.17 Write the equation that relates the standard cell potential to the standard free energy change for a reaction.

20.18 What is the equation that relates the equilibrium constant to the cell potential?

20.19 Show how the equation that relates the equilibrium constant to the cell potential (Equation 20.7) can be derived from the Nernst equation (Equation 20.8).

The Effect of Concentration on Cell Potential

20.20 The cell reaction during the discharge of a lead storage battery is

$$\mathrm{Pb}(s) + \mathrm{PbO}_2(s) + 2\mathrm{H}^+(aq) + 2\mathrm{HSO}_4^-(aq) \longrightarrow 2\mathrm{PbSO}_4(s) + 2\mathrm{H}_2\mathrm{O}$$

The standard cell potential is 2.05 V. What is the correct form of the Nernst equation for this reaction at 25 °C?

20.21 What is a concentration cell? Why is the E°_{cell} for such a cell equal to zero?

Practical Galvanic Cells

20.22 What are the anode and cathode reactions during the discharge of a lead storage battery? How can a battery produce a potential of 12 V if the cell reaction has a standard potential of only 2 V?

20.23 What are the anode and cathode reactions during the charging of a lead storage battery?

20.24 How is a hydrometer constructed? How does it measure density? Why can a hydrometer be used to check the state of charge of a lead storage battery?

20.25 What reactions occur at the electrodes in the ordinary dry cell?

20.26 What chemical reactions take place at the electrodes in an alkaline dry cell?

20.27 Give the half-cell reactions and the cell reaction that take place in a nicad battery during discharge. What are the reactions that take place during the charging of the cell?

20.28 How is hydrogen held as a reactant in a nickel–metal hydride battery? Write the chemical formula for a typical alloy used in this battery. What is the electrolyte?

20.29 What are the anode, cathode, and net cell reactions that take place in a nickel–metal hydride battery during discharge? What are the reactions when the battery is charged?

20.30 Give two reasons why lithium is such an attractive anode material for use in a battery. What are the problems associated with using lithium for this purpose?

20.31 What are the electrode materials in a typical primary lithium cell? Write the equations for the anode, cathode, and cell reactions.

20.32 What are the electrode materials in a typical lithium ion cell? Explain what happens when the cell is charged. Explain what happens when the cell is discharged.

20.33 Write the cathode, anode, and net cell reaction in a hydrogen–oxygen fuel cell.

20.34 What advantages do fuel cells offer over conventional means of obtaining electrical power by the combustion of fuels?

Electrolysis

20.35 What electrical charges do the anode and the cathode carry in an electrolytic cell? What does the term *inert electrode* mean?

20.36 Why must electrolysis reactions occur at the electrodes in order for electrolytic conduction to continue?

20.37 Why must NaCl be melted before it is electrolyzed to give Na and Cl_2? Write the anode, cathode, and overall cell reactions for the electrolysis of molten NaCl.

20.38 Write half-reactions for the oxidation and the reduction of water.

20.39 What happens to the pH of the solution near the cathode and anode during the electrolysis of K_2SO_4? What function does K_2SO_4 serve in the electrolysis of a K_2SO_4 solution?

Stoichiometric Relationships in Electrolysis

20.40 What is a *faraday*? What relationships relate faradays to current and time measurements?

20.41 Using the same current, which will require the greater length of time, depositing 0.10 mol Cu from a Cu^{2+} solution, or depositing 0.10 mol of Cr from a Cr^{3+} solution? Explain your reasoning.

20.42 An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Ag^{+}. In which cell will the larger number of moles of metal be deposited? Explain your answer.

20.43 An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Fe^{2+}. In which cell will the greater mass of metal be deposited? Explain your answer.

Applications of Electrolysis

20.44 What is *electroplating*? Sketch an apparatus to electroplate silver.

20.45 Describe the Hall–Héroult process for producing metallic aluminum. What half-reaction occurs at the anode? What half-reaction occurs at the cathode? What is the overall cell reaction?

20.46 In the Hall–Héroult process, why must the carbon anodes be replaced frequently?

20.47 How is metallic sodium produced? Write equations for the anode and cathode reactions. What are some uses of metallic sodium?

20.48 Describe the electrolytic refining of copper. What economic advantages offset the cost of electricity for this process? What chemical reactions occur at (a) the anode and (b) the cathode?

20.49 Describe the electrolysis of aqueous sodium chloride. How do the products of the electrolysis compare for stirred and unstirred reactions? Write chemical equations for the reactions that occur at the electrodes.

Review Problems

Cell Notation

20.50 Write the half-reactions and the balanced cell reaction for the following galvanic cells.

(a) $Cd(s) | Cd^{2+}(aq) || Au^{3+}(aq) | Au(s)$

(b) $Fe(s) | Fe^{2+}(aq) || Br_2(aq), Br^{-}(aq) | Pt(s)$

(c) $Cr(s) | Cr^{3+}(aq) || Cu^{2+}(aq) | Cu(s)$

OH **20.51** Write the half-reactions and the balanced cell reaction for the following galvanic cells.

(a) $Zn(s) | Zn^{2+}(aq) || Cr^{3+}(aq) | Cr(s)$

(b) $Pb(s), PbSO_4(s) | HSO_4^{-}(aq) ||$
$H^{+}(aq), HSO_4^{-}(aq) | PbO_2(s), PbSO_4(s)$

(c) $Mg(s) | Mg^{2+}(aq) || Sn^{2+}(aq) | Sn(s)$

20.52 Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.

(a) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O$

(b) $Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \longrightarrow Au(s) + 3Ag^+(aq)$

20.53 Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.

(a) $Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq)$

(b) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$

(c) $Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s)$

Reduction Potentials

20.54 For each pair of substances, use Table 20.1 to choose the better reducing agent.

(a) $Sn(s)$ or $Ag(s)$

(b) $Cl^-(aq)$ or $Br^-(aq)$

(c) $Co(s)$ or $Zn(s)$

(d) $I^-(aq)$ or $Au(s)$

20.55 For each pair of substances, use Table 20.1 to choose the better oxidizing agent.

(a) $NO_3^-(aq)$ or $MnO_4^-(aq)$

(b) $Au^{3+}(aq)$ or $Co^{2+}(aq)$

(c) $PbO_2(s)$ or $Cl_2(g)$

(d) $NiO_2(s)$ or $HOCl(aq)$

OH **20.56** Use the data in Table 20.1 to calculate the standard cell potential for each of the following reactions:

(a) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O$

(b) $Br_2(aq) + 2Cl^-(aq) \longrightarrow Cl_2(g) + 2Br^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \longrightarrow Au(s) + 3Ag^+(aq)$

20.57 Use the data in Table 20.1 to calculate the standard cell potential for each of the following reactions:

(a) $Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq)$

(b) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$

(c) $Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s)$

20.58 From the positions of the half-reactions in Table 20.1, determine whether the following reactions are spontaneous under standard state conditions.

(a) $2Au^{3+} + 6I^- \longrightarrow 3I_2 + 2Au$

(b) $H_2SO_3 + H_2O + Br_2 \longrightarrow 4H^+ + SO_4^{2-} + 2Br^-$

(c) $3Ca + 2Cr^{3+} \longrightarrow 2Cr + 3Ca^{2+}$

20.59 Use the data in Table 20.1 to determine which of the following reactions should occur spontaneously under standard state conditions.

(a) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

(b) $3Fe^{2+} + 2NO + 4H_2O \longrightarrow 3Fe + 2NO_3^- + 8H^+$

(c) $Ni^{2+} + Fe \longrightarrow Fe^{2+} + Ni$

ILW **20.60** From the half-reactions below, determine the cell reaction and standard cell potential.

$$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O \qquad E^\circ_{BrO_3^-} = 1.44\ V$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\circ_{I_2} = 0.54\ V$$

20.61 What is the standard cell potential and the net reaction in a galvanic cell that has the following half-reactions?

$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O \qquad E^\circ_{MnO_2} = 1.23\ V$$

$$PbCl_2 + 2e^- \rightleftharpoons Pb + 2Cl^- \qquad E^\circ_{PbCl_2} = -0.27\ V$$

OH **20.62** What will be the spontaneous reaction among H_2SO_3, $S_2O_3^{2-}$, HOCl, and Cl_2? The half-reactions involved are

$$2H_2SO_3 + 2H^+ + 4e^- \rightleftharpoons S_2O_3^{2-} + 3H_2O \qquad E^\circ_{H_2SO_3} = 0.40\ V$$

$$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O \qquad E^\circ_{HOCl} = 1.63\ V$$

20.63 What will be the spontaneous reaction among Br_2, I_2, Br^-, and I^- ?

20.64 Will the following reaction occur spontaneously under standard state conditions?

$$SO_4^{2-} + 4H^+ + 2I^- \longrightarrow H_2SO_3 + I_2 + H_2O$$

Use E°_{cell} calculated from data in Table 20.1 to answer this question.

20.65 Determine whether the reaction

$$S_2O_8^{2-} + Ni(OH)_2 + 2OH^- \longrightarrow 2SO_4^{2-} + NiO_2 + 2H_2O$$

will occur spontaneously under standard state conditions. Use E°_{cell} calculated from the data below to answer the question.

$$NiO_2 + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2 + 2OH^- \qquad E^\circ_{NiO_2} = 0.49\ V$$

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-} \qquad E^\circ_{S_2O_8^{2-}} = 2.01\ V$$

Cell Potentials and Thermodynamics

ILW **20.66** Calculate ΔG° for the following reaction *as written*

$$2Br^- + I_2 \longrightarrow 2I^- + Br_2$$

OH **20.67** Calculate ΔG° for the reaction

$$2MnO_4^- + 6H^+ + 5HCHO_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5CO_2$$

for which $E^\circ_{cell} = 1.69$ V.

20.68 Given the following half-reactions and their standard reduction potentials,

$$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O \qquad E^\circ_{ClO_3^-} = 0.47\ V$$

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-} \qquad E^\circ_{S_2O_8^{2-}} = 2.01\ V$$

calculate **(a)** E°_{cell}, **(b)** ΔG° for the cell reaction, and **(c)** the value of K_c for the cell reaction.

20.69 Calculate K_c for the system $Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$. Use the data in Table 20.1 and assume $T = 298$ K.

20.70 The system $2AgI + Sn \rightleftharpoons Sn^{2+} + 2Ag + 2I^-$ has a calculated $E^\circ_{\text{cell}} = -0.015$ V. What is the value of K_c for this system?

20.71 Determine the value of K_c at 25 °C for the reaction

$$2H_2O + 2Cl_2 \rightleftharpoons 4H^+ + 4Cl^- + O_2$$

Cell Potentials and Concentration

20.72 The cell reaction

$$NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$$

has $E^\circ_{\text{cell}} = 2.48$ V. What will be the cell potential at a pH of 2.00 when the concentrations of Ni^{2+} and Ag^+ are each 0.030 *M*?

20.73 The $E^\circ_{\text{cell}} = 0.135$ V for the reaction

$$3I_2(s) + 5Cr_2O_7^{\ 2-}(aq) + 34H^+ \longrightarrow 6IO_3^{\ -}(aq) + 10Cr^{3+}(aq) + 17H_2O$$

What is E_{cell} if $[Cr_2O_7^{\ 2-}] = 0.010$ *M*, $[H^+] = 0.10$ *M*, $[IO_3^{\ -}] = 0.00010$ *M*, and $[Cr^{3+}] = 0.0010$ *M*?

OH ***20.74** A cell was set up having the following reaction.

$$Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s) \qquad E^\circ_{\text{cell}} = 1.97 \text{ V}$$

The magnesium electrode was dipped into a 1.00 *M* solution of $MgSO_4$ and the cadmium electrode was dipped into a solution of unknown Cd^{2+} concentration. The potential of the cell was measured to be 1.54 V. What was the unknown Cd^{2+} concentration?

***20.75** A silver wire coated with AgCl is sensitive to the presence of chloride ion because of the half-cell reaction

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad E^\circ_{\text{AgCl}} = 0.2223 \text{ V}$$

A student, wishing to measure the chloride ion concentration in a number of water samples, constructed a galvanic cell using the AgCl electrode as one half-cell and a copper wire dipping into 1.00 *M* $CuSO_4$ solution as the other half-cell. In one analysis, the potential of the cell was measured to be 0.0895 V with the copper half-cell serving as the cathode. What was the chloride ion concentration in the water? (Take $E^\circ_{Cu^{2+}} = 0.3419$ V.)

***20.76** At 25 °C, a galvanic cell was set up having the following half-reactions.

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^\circ_{Fe^{2+}} = -0.447 \text{ V}$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ_{Cu^{2+}} = +0.3419 \text{ V}$$

The copper half-cell contained 100 mL of 1.00 *M* $CuSO_4$. The iron half-cell contained 50.0 mL of 0.100 *M* $FeSO_4$. To the iron half-cell was added 50.0 mL of 0.500 *M* NaOH solution. The mixture was stirred and the cell potential was measured to be 1.175 V. Calculate the concentration of Fe^{2+} in the solution.

***20.77** Suppose a galvanic cell was constructed at 25 °C using a Cu/Cu^{2+} half-cell (in which the molar concentration of Cu^{2+} was 1.00 *M*) and a hydrogen electrode having a partial pressure of H_2 equal to 1 atm. The hydrogen electrode dips into a solution of unknown hydrogen ion concentration, and the two half-cells are connected by a salt bridge. The precise value of $E^\circ_{Cu^{2+}}$ is +0.3419 V.

(a) Derive an equation for the pH of the solution with the unknown hydrogen ion concentration, expressed in terms of E_{cell} and E°_{cell}.

(b) If the pH of the solution were 5.15, what would be the observed potential of the cell?

(c) If the potential of the cell were 0.645 V, what would be the pH of the solution?

***20.78** What is the potential of a concentration cell at 25.0 °C if it consists of silver electrodes dipping into two different solutions of $AgNO_3$, one with a concentration of 0.015 *M* and the other with a concentration of 0.50 *M*? What would be the potential of the cell if the temperature of the cell were 75 °C?

***20.79** What is the potential of a concentration cell at 25.0 °C if it consists of copper electrodes dipping into two different solutions of $Cu(NO_3)_2$, one with a concentration of 0.015 *M* and the other with a concentration of 0.50 *M*? What would be the potential of the cell if the temperature of the cell were 75 °C?

Quantitative Aspects of Electrochemical Reactions

20.80 How many moles of electrons are required to: **(a)** Reduce 0.20 mol Fe^{2+} to Fe? **(b)** Oxidize 0.70 mol Cl^- to Cl_2? **(c)** Reduce 1.50 mol Cr^{3+} to Cr? **(d)** Oxidize 1.0×10^{-2} mol Mn^{2+} to $MnO_4^{\ -}$?

20.81 How many moles of electrons are required to: **(a)** Produce 5.00 g Mg from molten $MgCl_2$? **(b)** Form 41.0 g Cu from a $CuSO_4$ solution?

ILW **20.82** How many grams of $Fe(OH)_2$ are produced at an iron anode when a basic solution undergoes electrolysis at a current of 8.00 A for 12.0 min?

20.83 How many grams of Cl_2 would be produced in the electrolysis of molten NaCl by a current of 4.25 A for 35.0 min?

ILW **20.84** How many hours would it take to produce 75.0 g of metallic chromium by the electrolytic reduction of Cr^{3+} with a current of 2.25 A?

20.85 How many hours would it take to generate 35.0 g of lead from $PbSO_4$ during the charging of a lead storage battery using a current of 1.50 A? The half-reaction is

$$Pb + HSO_4^{\ -} \longrightarrow PbSO_4 + H^+ + 2e^-$$

OH **20.86** How many amperes would be needed to produce 60.0 g of magnesium during the electrolysis of molten $MgCl_2$ in 2.00 hr?

20.87 A large electrolysis cell that produces metallic aluminum from Al_2O_3 by the Hall–Héroult process is capable of yielding 900 lb (409 kg) of aluminum in 24 hr. What current is required?

***20.88** The electrolysis of 250 mL of a brine solution (NaCl) was carried out for a period of 20.00 min with a current of 2.00 A in an apparatus that prevented Cl_2 from reacting with other products of the electrolysis. What is the concentration of hydroxide ions in the solution?

***20.89** A 100.0 mL sample of 2.00 *M* NaCl was electrolyzed for a period of 25.0 min with a current of 1.45 amperes, with stirring. What is the concentration of sodium hypochlorite produced?

Predicting Electrolysis Reactions

20.90 If electrolysis is carried out on an aqueous solution of aluminum sulfate, what products are expected at the electrodes? Write the equation for the net cell reaction.

20.91 If electrolysis is carried out on an aqueous solution of cadmium iodide, what products are expected at the electrodes? Write the equation for the net cell reaction.

OH 20.92 What products would we expect at the electrodes if a solution containing both KBr and $CuSO_4$ were electrolyzed? Write the equation for the net cell reaction.

20.93 What products would we expect at the electrodes if a solution containing both $BaCl_2$ and CuI_2 were electrolyzed? Write the equation for the net cell reaction.

20.94 Using Table 20.1, list the ions in aqueous solution that we would not expect to be reduced at the cathode.

20.95 Using Table 20.1, list the ions, in aqueous solution, that we would not expect to be oxidized at the anode.

Additional Exercises

***20.96** A watt is a unit of electrical power and is equal to one joule per second (1 watt = 1 J s^{-1}). How many hours can a calculator drawing 2.0×10^{-3} watt be operated by a mercury battery having a cell potential equal to 1.34 V if a mass of 1.00 g of HgO is available at the cathode? The cell reaction is

$$\text{HgO}(s) + \text{Zn}(s) \longrightarrow \text{ZnO}(s) + \text{Hg}(l)$$

***20.97** Suppose that a galvanic cell were set up having the net cell reaction

$$\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$$

The Ag^+ and Zn^{2+} concentrations in their respective half-cells initially are 1.00 *M*, and each half-cell contains 100 mL of electrolyte solution. If this cell delivers current at a constant rate of 0.10 A, what will the cell potential be after 15.00 hr?

***20.98** The value of K_{sp} for AgBr is 5.4×10^{-13}. What will be the potential of a cell constructed of a standard hydrogen electrode as one half-cell and a silver wire coated with AgBr dipping into 0.10 *M* HBr as the other half-cell. For the Ag/AgBr electrode,

$$\text{AgBr}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Br}^-(aq) \qquad E^\circ_{\text{AgBr}} = +0.070 \text{ V}$$

***20.99** A student set up an electrolysis apparatus and passed a current of 1.22 A through a 3 *M* H_2SO_4 solution for 30.0 min. The H_2 formed at the cathode was collected and found to have a volume, over water at 27 °C, of 288 mL at a total pressure of 767 torr. Use these data to calculate the charge on the electron, expressed in coulombs.

***20.100** A hydrogen electrode is immersed in a 0.10 *M* solution of acetic acid at 25 °C. This electrode is connected to another consisting of an iron nail dipping into 0.10 *M* $FeCl_2$. What will be the measured potential of this cell? Assume $P_{H_2} = 1.00$ atm.

***20.101** What current would be required to deposit 1.00 m^2 of chrome plate having a thickness of 0.050 mm in 4.50 hr from a solution of H_2CrO_4? The density of chromium is 7.19 g cm^{-3}.

***20.102** A solution containing vanadium (chemical symbol V) in an unknown oxidation state was electrolyzed with a current of 1.50 A for 30.0 min. It was found that 0.475 g of V was deposited on the cathode. What was the original oxidation state of the vanadium ion?

***20.103** Consider the reduction potentials of the following sets of substances: **(a)** F_2, Cl_2, Br_2, and I_2 **(b)** Li^+, Na^+, K^+, Rb^-, and Cs^+ **(c)** Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. How do the reduction potentials correlate with properties such as electron affinities, ionization energies, and electronegativities? If necessary, suggest why a correlation does not occur.

***20.104** An Ag/AgCl electrode dipping into 1.00 *M* HCl has a standard reduction potential of +0.2223 V. The half-reaction is

$$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-(aq)$$

A second Ag/AgCl electrode is dipped into a solution containing Cl^- at an unknown concentration. The cell generates a potential of 0.0478 V, with the electrode in the solution of unknown concentration having a negative charge. What is the molar concentration of Cl^- in the unknown solution?

20.105 Consider the following galvanic cell:

$$\text{Ag}(s) \,|\, \text{Ag}^+(3.0 \times 10^{-4}\, M) \,\|\, \text{Fe}^{3+}(1.1 \times 10^{-3}\, M), \text{Fe}^{2+}(0.040\, M) \,|\, \text{Pt}(s)$$

Calculate the cell potential. Determine the sign of the electrodes in the cell. Write the equation for the spontaneous cell reaction.

Multi-Concept Problems

***20.106** The electrolysis of 0.250 L of a brine solution (NaCl) was carried out for a period of 20.00 min with a current of 2.00 A in an apparatus that prevented Cl_2 from reacting with other products of the electrolysis. The resulting solution was titrated with 0.620 *M* HCl. How many mL of the HCl solution was required for the titration?

OH ***20.107** A solution of NaCl in water was electrolyzed with a current of 2.50 A for 15.0 min. How many milliliters of dry Cl_2 gas would be formed if it was collected over water at 25 °C and a total pressure of 750 torr?

***20.108** How many milliliters of dry gaseous H_2, measured at 20.0 °C and 735 torr, would be produced at the cathode in the electrolysis of dilute H_2SO_4 with a current of 0.750 A for 15.00 min?

***20.109** At 25 °C, a galvanic cell was set up having the following half-reactions.

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^\circ_{Fe^{2+}} = -0.447\ V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ_{Cu^{2+}} = +0.3419\ V$$

The copper half-cell contained 100 mL of 1.00 *M* $CuSO_4$. The iron half-cell contained 50.0 mL of 0.100 *M* $FeSO_4$. To the iron half-cell was added 50.0 mL of 0.500 *M* NaOH solution. The mixture was stirred and the cell potential was measured to be 1.175 V. Calculate the value of K_{sp} for $Fe(OH)_2$.

***20.110** Given the following reduction half-reactions and their standard potentials, what is the molar solubility of silver bromide?

$$Ag^+ + e^- \longrightarrow Ag \qquad E^\circ_{Ag^+} = +0.80\ V$$
$$AgBr + e^- \longrightarrow Ag + Br^- \qquad E^\circ_{AgBr} = +0.07\ V$$

***20.111** The normal range of chloride ions in blood serum (serum is the fluid left after the red blood cells clot) ranges from 0.096 to 0.106 *M*. An electrolysis apparatus can be set up to generate silver ions from a silver anode to precipitate the chloride ions. If the current used in the experiment is 0.500 ampere and if 3.00 mL of serum is transferred to the electrolysis cell, what range of time, in seconds, will a normal sample take to precipitate all of the chloride ions?

***20.112** An unstirred solution of 2.00 *M* NaCl was electrolyzed for a period of 25.0 min and then titrated with 0.250 *M* HCl. The titration required 15.5 mL of the acid. What was the average current in amperes during the electrolysis?

20.113 What masses of H_2 and O_2 in grams would have to react each second in a fuel cell at 110 °C to provide 1.00 kilowatt (kW) of power if we assume a thermodynamic efficiency of 70%? (*Hint*: Use data in Chapters 6 and 18 to compute the value of ΔG° for the reaction $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ at 110 °C. 1 watt = 1 J s^{-1}.)

Exercises in Critical Thinking

20.114 In biochemical systems, the normal standard state that requires $[H^+] = 1.00\ M$ is not realistic. **(a)** Which half-reactions in Table 20.1 will have different potentials if pH = 7.00 is defined as the standard state for hydronium ions? **(b)** What will the new standard reduction potentials be at pH = 7.00 for these reactions? These are called $E^{\circ\prime}_{cell}$ with the prime indicating the potential at pH = 7.00.

20.115 Calculate a new version of Table 20.1 using the lithium half-reaction to define zero. Does this change the results of any problems involving standard cell potentials?

20.116 In Problem 20.79, the potential at 75 °C was calculated. Does the change in molarity of the solutions, due to the change in density of water, have an effect on the potentials?

20.117 There are a variety of methods available for generating electricity. List as many methods as you can. Rank each of these methods based on your knowledge of **(a)** the efficiency of the method and **(b)** the environmental pollution caused by each method.

20.118 Using the cost of electricity in your area, how much will it cost to produce a case of 24 soda cans, each weighing 0.45 ounce? Assume that alternating current can be converted to direct current with 100% efficiency.

***20.119** Most flashlights use two or more batteries in series. Use the concepts of galvanic cells in this chapter to explain why a flashlight with two new batteries and one "dead" battery will give only a dim light if any light is obtained at all.

***20.120** If two electrolytic cells are placed in series, the same number of electrons must pass through both cells. One student argues you can get twice as much product if two cells are placed in series compared to a single cell and therefore the cost of production (i.e., the cost of electricity) will decrease greatly and profits will increase. Is the student correct? Explain your reasoning based on the principles of electrochemistry.

Chapters 17–20

Bringing It Together

Again we pause to provide you with an opportunity to see how well you have grasped concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–16. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. At 60 °C, $K_w = 9.5 \times 10^{-14}$. What is the pH of pure water at this temperature? Why can we say that this water is neither acidic nor basic?

2. At 25 °C, the water in a natural pool of water in one of the western states was found to contain hydroxide ions at a concentration of 4.7×10^{-7} g OH^- per liter. Calculate the pH of this water and state if it is acidic, basic, or neutral.

3. The first antiseptic to be used in surgical operating rooms was phenol, C_6H_5OH, a weak acid and a potent bactericide. A 0.550 *M* solution of phenol in water was found to have a pH of 5.07.

(a) Write the chemical equation for the equilibrium involving C_6H_5OH in the solution.

(b) Write the equilibrium law corresponding to K_a for C_6H_5OH.

(c) Calculate the values of K_a and pK_a for phenol.

(d) Calculate the values of K_b and pK_b for the phenoxide ion, $C_6H_5O^-$.

4. The pK_a of saccharin, $HC_7H_3SO_3$, a sweetening agent, is 11.68.

(a) What is the pK_b of the saccharinate ion, $C_7H_3SO_3^-$?

(b) Does a solution of sodium saccharinate in water have a pH of 7, or is the solution acidic or basic? If the pH is not 7, calculate the pH of a 0.010 *M* solution of sodium saccharinate in water.

5. At 25 °C the value of K_b for codeine, a pain-killing drug, is 1.63×10^{-6}. Calculate the pH of a 0.0115 *M* solution of codeine in water.

6. Methylamine, CH_3NH_2, is a weak base. Write the chemical equation for the equilibrium that occurs in an aqueous solution of this solute. Write the equilibrium law corresponding to K_b for CH_3NH_2.

7. The pK_b of methylamine, CH_3NH_2, is 3.36. Calculate the pK_a of its conjugate acid, $CH_3NH_3^+$.

8. Ascorbic acid, $H_2C_6H_6O_6$, is a diprotic acid usually known as vitamin C. For this acid, pK_{a_1} is 4.10 and pK_{a_2} is 11.80. When 125 mL of a solution of ascorbic acid was evaporated to dryness, the residue of pure ascorbic acid had a mass of 3.12 g.

(a) Calculate the molar concentration of ascorbic acid in the solution before it was evaporated.

(b) Calculate the pH of the solution and the molar concentration of the ascorbate ion, $C_6H_6O_6^{2-}$, before the solution was evaporated.

9. What ratio of molar concentrations of sodium acetate to acetic acid can buffer a solution at a pH of 4.50?

10. Write a chemical equation for the reaction that would occur in a buffer composed of $NaC_2H_3O_2$ and $HC_2H_3O_2$ if

(a) some HCl were added.

(b) some NaOH were added.

11. If 0.020 mol of NaOH were added to 500 mL of a sodium acetate–acetic acid buffer that contains 0.10 *M* $NaC_2H_3O_2$ and 0.15 *M* $HC_2H_3O_2$, by how many pH units will the pH of the buffer change?

12. A biology experiment requires the use of a nutrient fluid buffered at a pH of 4.85, and 625 mL of this solution is needed. It has to be buffered to be able to hold the pH to within ±0.10 pH unit of 5.00 even if 5.00×10^{-3} mol of OH^- or 5.00×10^{-3} mol of H^+ ion enter.

(a) Using tabulated data, pick the best acid and its sodium salt that could be used to prepare this solution.

(b) Calculate the minimum number of grams of the pure acid and its salt that are needed to prepare this buffer solution.

(c) What are the molar concentrations of the acid and of its salt in this solution?

13. Would each of the following aqueous solutions test acidic, basic, or neutral? (Assume that each is at least 0.2 *M*.)
(a) KNO_3, (b) $CrCl_3$, (c) NH_4I, (d) K_2HPO_4

14. When 50.00 mL of an acid with a concentration of 0.115 *M* (for which $pK_a = 4.87$) is titrated with 0.100 *M* NaOH, what is the pH at the equivalence point? What would be a good indicator for this titration?

15. Calculate the pH of a 0.050 *M* solution of sodium ascorbate, $NaC_6H_6O_6$. For ascorbic acid, $H_2C_6H_6O_6$, $K_{a_1} = 8.0 \times 10^{-5}$ and $K_{a_2} = 1.6 \times 10^{-12}$.

16. When 25.0 mL of 0.100 *M* NaOH was added to 50.0 mL of a 0.100 *M* solution of a weak acid, HX, the pH of the mixture reached a value of 3.56. What is the value of K_a for the weak acid?

17. How many grams of solid NaOH would have to be added to 100 mL of a 0.100 *M* solution of NH_4Cl to give a mixture with a pH of 9.26?

18. The molar solubility of silver chromate, Ag_2CrO_4, in water is 6.5×10^{-5} *M*. What is K_{sp} for Ag_2CrO_4?

19. What is the pH of a saturated solution of $Mg(OH)_2$?

20. What is the solubility of $Fe(OH)_2$ in grams per liter if the solution is buffered to a pH of 10.00?

21. Which of the following states has the greatest entropy?

(a) $2H_2O(l)$,
(b) $2H_2O(s)$,
(c) $2H_2(l) + O_2(g)$,
(d) $2H_2(g) + O_2(g)$,
(e) $4H(g) + 2O(g)$

22. Suppose 30.0 mL of a solution containing 1.040 g $Pb(NO_3)_2$ is added to 20.0 mL of 0.500 *M* KI.

(a) How many grams of PbI_2 will be formed?

(b) What will the molar concentrations of all the ions be in the mixture after equilibrium has been reached?

(c) If a lead electrode is immersed in the mixture and the resulting half-cell is connected to another half-cell composed of a copper electrode dipping into 1.00 *M* $CuSO_4$, what will be the potential of the cell?

23. How many moles of NH_3 must be added to 1.00 L of solution to dissolve 1.00 g of $CuCO_3$? For $CuCO_3$, $K_{sp} = 2.5 \times 10^{-10}$. Ignore hydrolysis of $CO_3{}^{2-}$, but consider the formation of the complex ion, $Cu(NH_3)_4{}^{2+}$.

24. Over what pH range must a solution be buffered to achieve a selective separation of the carbonates of barium, $BaCO_3$, ($K_{sp} = 2.6 \times 10^{-9}$), and lead, $PbCO_3$ ($K_{sp} = 7.4 \times 10^{-14}$)? The solution is initially 0.010 *M* in Ba^{2+} and 0.010 *M* in Pb^{2+}.

25. A solution containing 0.10 *M* Pb^{2+} and 0.10 *M* Ni^{2+} is to be saturated with H_2S. What range of pH values could this solution have so that when the procedure is completed one of the ions remains in solution while the other is precipitated as its sulfide?

26. A solution that contains 0.10 *M* Fe^{2+} and 0.10 *M* Sn^{2+} is maintained at a pH of 3.00 while H_2S is gradually added to it. What will be the concentration of Sn^{2+} in the solution when FeS just begins to precipitate?

27. A metal sulfide *M*S has a value of K_{sp} of 4.0×10^{-29}. (a) What is the value of K_{spa} for this compound? (b) Calculate the molar solubility of *M*S in 0.30 *M* HCl. (c) Does *M*S fall into cation group 2 or cation group 3?

28. Use thermodynamic data and other information available in previous chapters to calculate K_c at 200 °C for the reaction

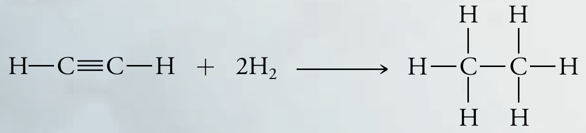
$$3NO(g) \rightleftharpoons NO_2(g) + N_2O(g)$$

29. Suppose 4.56 g of CH_4 and 8.67 g of HCl were placed in a 2.00 L container at 200 °C where the following equilibrium is established.

$$CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$$

Use thermodynamic data and other information available in this book to calculate the concentrations of all the gases at equilibrium.

30. Use bond energies to calculate the approximate energy that would be absorbed or given off in the formation of 25.0 g of C_2H_6 by the following reaction in the gas phase.



$$H{-}C{\equiv}C{-}H + 2H_2 \longrightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H$$

31. Consider an electrolytic cell in which 250 mL of a concentrated solution of NaCl is undergoing electrolysis.

(a) What will be the pH of the solution if the electrolysis is carried out for 20.0 minutes using a current of 1.00 A?

(b) How many milliliters of H_2, measured at STP, would be evolved if the cell were operated at 5.00 A for 10.0 minutes?

32. Sketch a diagram of a galvanic cell consisting of a copper electrode dipping into 1.00 *M* $CuSO_4$ solution and an iron electrode dipping into 1.00 *M* $FeSO_4$ solution.

(a) Identify the cathode and the anode. Indicate the charge carried by each.

(b) Write the equation for the net cell reaction.

(c) Describe the cell by writing its standard cell notation.

(d) What is the potential of the cell?

(e) If the cell contains 100 mL of each solution and is operated for a period of 50.0 hr at a constant current of 0.10 A, what will be the cell potential at this point?

33. A galvanic cell was constructed in which one half-cell consists of a silver electrode coated with silver chloride dipping into a solution that contains 0.050 *M* Cl^- and the second half-cell consists of a nickel electrode dipping into a solution buffered to a pH of 12.00 that contains insoluble $Ni(OH)_2$. The half-cell reactions and their reduction potentials are

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq) \qquad E° = +0.222 \text{ V}$$

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E° = -0.257 \text{ V}$$

(a) Write the equation for the spontaneous cell reaction.

(b) Calculate E_{cell} for the galvanic cell described above.

34. Suppose a galvanic cell was established using the following cell reaction,

$$Cu(s) + 2Ag^+(0.100\ M) \longrightarrow Cu^{2+}(0.200\ M) + 2Ag(s)$$

What is the potential of the cell at 25 °C? How long would it take at a constant current of 0.10 A for the potential to drop by 10%? By how many grams will the total mass of the two electrodes change during this time period? Will the entire mass of the galvanic cell change?

21

Nuclear Reactions and Their Role in Chemistry

Chapter Outline

21.1 | Conservation of Mass and Energy
21.2 | Nuclear Binding Energy
21.3 | Radioactivity
21.4 | Band of Stability
21.5 | Transmutation
21.6 | Measuring Radioactivity
21.7 | Medical and Analytical Applications of Radionuclides
21.8 | Nuclear Fission and Fusion

What is the Asian brown cloud? This large brown cloud of pollution hangs over southeast Asia from January to March. While atmospheric chemists know it is formed from particulates created when fuels are not completely burned, they are also interested in the source of the fuels. By using the nuclear reactions of the elements of the Asian brown cloud, these scientists are able to determine the age of the material that was burned to form the cloud. Johannes Mann/©Corbis

This Chapter in Context

From the standpoint of chemistry, our interest in the atomic nucleus stems primarily from its role in determining the number and energies of an atom's electrons. This is because it is the electron distribution in an atom that controls chemical properties. Although the nuclei of most isotopes are exceptionally stable, many of the elements also have one or more isotopes with unstable nuclei that have unique properties which make them particularly useful and interesting. These unstable nuclei are able to undergo *nuclear reactions*, and tend to emit radiation consisting of particles and/or energy. In the pages ahead you will learn about the different kinds of nuclear radiation, how this radiation is detected and measured, and how the properties of unstable nuclei can be applied to practical problems.

One of the benefits of studying nuclear transformations is an understanding of the enormous amounts of energy associated with certain nuclear changes. As you study this chapter you will come to appreciate the origin of the energy given off by stars, including our own sun. You will also learn how nuclear reactors work and how nuclear reactions have been applied to produce nuclear weapons.

21.1 | Conservation of Mass and Energy

Changes involving unstable atomic nuclei generally involve large amounts of energy, amounts that are considerably greater than in chemical reactions. To understand how these energy changes arise, we begin our study by reexamining two physical laws that, until this chapter, have been assumed to be separate and independent—namely, the laws of conservation of energy and conservation of mass. They may be safely treated as distinct for chemical reactions but not for nuclear reactions. These two laws, however, are only different aspects of a deeper, more general law.

As atomic and nuclear physics developed in the early 1900s, physicists realized that the mass of a particle cannot be treated as a constant in all circumstances. The mass, m, of a particle depends on the particle's velocity, v, relative to the observer. A particle's mass is related to this velocity, and to the velocity of light, c, by Equation 21.1.

$$m = \frac{m_0}{\sqrt{1 - (v/c)^2}} \qquad \textbf{(21.1)}$$

■ $c = 2.99792458 \times 10^8$ m s^{-1}, the speed of light.

Notice what happens when v is zero and the particle has no velocity relative to the observer. The ratio v/c is then zero, the entire denominator reduces to a value of 1, and Equation 21.1 becomes

$$m = m_0$$

Thus the symbol m_0 stands for the particle's *rest mass*.

Rest mass is what we measure in all lab operations, because any object, like a chemical sample, is either at rest (from our viewpoint) or is not moving extraordinarily rapidly. Only as the particle's velocity approaches the speed of light, c, does the v/c term in Equation 21.1 become important. As v approaches c, the ratio v/c approaches 1, and so $[1 - (v/c)^2]$ gets closer and closer to 0. The whole denominator, in other words, approaches a value of 0. If it actually reached 0, then m, which would be $(m_0 \div 0)$, would become infinity. In other words, the mass, m, of the particle moving at the velocity of light would be infinitely great, a physical impossibility. Thus the speed of light is seen as the absolute upper limit of the speed that any particle can approach.

■ Even at $v = 1000$ m s^{-1} (about 2250 mph), the denominator (not rounded) is 0.99999333, or within 7×10^{-4}% of 1.

At the velocities of everyday experience, the mass of anything calculated by Equation 21.1 equals the rest mass to four or five significant figures. The difference cannot be detected by weighing devices. Thus, in all of our normal work, mass appears to be conserved, and the law of conservation of mass functions this way in chemistry.

Practice Exercises

21.1 | What is the mass of a golf ball traveling at 75 m s^{-1}? The rest mass of a golf ball is 45.9 g, as regulated by the United States Golf Association. (*Hint*: How does the velocity of the golf ball affect the speed?)

21.2 | What is the mass of the same golf ball in Practice Exercise 21.1 if the velocity of the ball is increased to 7.5×10^6 m s^{-1}?

Law of Conservation of Mass–Energy

We know that matter cannot appear from nothing, so the extra mass an object acquires as it goes faster must come from the energy supplied to increase the object's velocity. Physicists, therefore, realized that mass and energy are interconvertible and that in the world of high-energy physics, the laws of conservation of mass and conservation of energy are not separate and independent. What emerged was a single law now called the **law of conservation of mass–energy.**

> **Law of Conservation of Mass–Energy**
> The sum of all of the energy in the universe and of all of the mass (expressed as an equivalent in energy) is a constant.

The Einstein Equation

■ The Einstein equation is given as $E = mc^2$ in the popular press.

TOOLS
Einstein equation

Albert Einstein was able to show that when mass converts to energy, the change in energy, ΔE, is related to the change in rest mass, Δm_0, by the following equation, now called the **Einstein equation:**

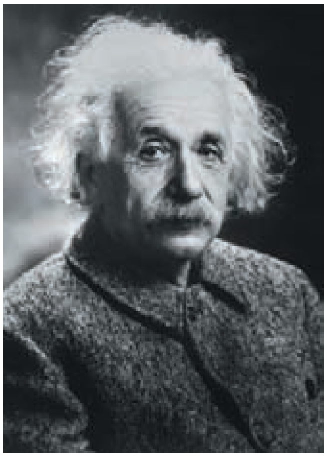
$$\Delta E = \Delta m_0 c^2 \qquad (21.2)$$

Again, c is the velocity of light, 3.00×10^8 m s^{-1}.

Because the velocity of light is very large, even if an energy change is enormous, the change in mass, Δm_0, is extremely small. For example, the combustion of methane releases considerable heat per mole:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890 \text{ kJ}$$

The release of 890 kJ of heat energy corresponds to a loss of mass, which by the Einstein equation equals a loss of 9.89 ng. This is about 1×10^{-7}% of the total mass of 1 mol of CH_4 and 2 mol of O_2. Such a tiny change in mass is not detectable by laboratory balances, so for all practical purposes, mass is conserved. Although the Einstein equation has no direct applications in chemistry involving the rearrangement of electrons in chemical reactions, its importance became clear when atomic fission (i.e., the breaking apart of heavy atoms to form lighter fragments) was first observed in 1939.



Albert Einstein (1879–1955); Nobel Prize, 1921 (physics) *(Photo Researchers)*

21.2 | Nuclear Binding Energy

As we will discuss further in Section 21.3, an atomic nucleus is held together by extremely powerful forces of attraction that are able to overcome the repulsions between protons. To break a nucleus into its individual **nucleons**—that is, protons and neutrons—therefore requires an enormous input of energy. This energy is called the **nuclear binding energy.**

Absorption of the binding energy would produce the individual nucleons that had made up the nucleus. These nucleons would now carry extra mass corresponding to the mass-equivalent of the energy they had absorbed. If we add up their masses, the sum should be larger than the mass of the nucleus from which they had come. And this is exactly what is observed. *For a given atomic nucleus, the sum of the rest masses of all of its nucleons is always a little larger than the actual mass of the nucleus.* The mass difference is called the **mass defect**, and its energy equivalance is the nuclear binding energy.

Keep in mind that nuclear binding energy is not energy actually possessed by the nucleus but is, instead, the energy the nucleus would have to absorb to break apart. Thus, the *higher* the binding energy, the *more stable* is the nucleus.

Calculating Nuclear Binding Energies

We can calculate nuclear binding energy with the Einstein equation, using helium-4 as an example. The rest mass of an isolated proton is 1.0072764669 u and that of a neutron is 1.0086649156 u. Helium-4 has atomic number 2, so its nucleus consists of four nucleons (two protons and two neutrons). The rest mass of one helium-4 nucleus is known to be 4.0015061792 u. However, the sum of the rest masses of its four separated nucleons is slightly more, 4.0318827650 u, which we can show as follows:

$$\begin{aligned}\text{For 2 protons: } 2 \times 1.0072764669 \text{ u} &= 2.0145529338 \text{ u} \\ \text{For 2 neutrons: } 2 \times 1.0086649156 \text{ u} &= \underline{2.0173298312 \text{ u}} \\ \text{Total rest mass of nucleons in } {}^{4}\text{He} &= 4.0318827650 \text{ u}\end{aligned}$$

The mass defect, the difference between the calculated and measured rest masses for the helium-4 nucleus, is 0.030375858 u:

$$\underset{\text{mass of the 4 nucleons}}{4.0318827650 \text{ u}} - \underset{\text{mass of nucleus}}{4.0015061792 \text{ u}} = \underset{\text{mass defect}}{0.030375858 \text{ u}}$$

Using Einstein's equation, let's calculate to four significant figures the nuclear binding energy that is equivalent to the mass defect for the ^{4}He nucleus. We will round the mass defect to 0.03038 u. To obtain the energy in joules, we have to remember that 1 J = 1 kg m^{2} s^{-2}, so the mass in atomic mass units (u) must be converted to kilograms. The table of constants inside the rear cover of the book gives 1 u = $1.66053878 \times 10^{-24}$ g, which equals $1.66053878 \times 10^{-27}$ kg. Substituting into the Einstein equation gives

$$\begin{aligned}\Delta E = \Delta mc^2 &= \underbrace{(0.03038 \cancel{\text{u}}) \times \frac{1.660653878 \times 10^{-27} \text{ kg}}{1 \cancel{\text{u}}}}_{\Delta m \text{ (in kg)}} \times \underbrace{(2.9979 \times 10^{8} \text{ m s}^{-1})^2}_{c^2} \\ &= 4.534 \times 10^{-12} \text{ kg m}^2 \text{ s}^{-2} \\ &= 4.534 \times 10^{-12} \text{ J}\end{aligned}$$

There are four nucleons in the helium-4 nucleus, so the binding energy *per* nucleon is (4.534×10^{-12} J/4 nucleons) or 1.134×10^{-12} J/nucleon.

The formation of just one nucleus of ^{4}He releases 4.534×10^{-12} J, which is a very small amount of energy. If we could make Avogadro's number or 1 mol of ^{4}He nuclei (with a total mass of only 4 g), the net release of energy would be

$$(6.022 \times 10^{23} \text{ nuclei}) \times (4.534 \times 10^{-12} \text{ J/nucleus}) = 2.731 \times 10^{12} \text{ J}$$

This is a huge amount of energy from forming only 4 g of helium. It could keep a 100 watt incandescent light bulb lit for nearly 900 years!

Practice Exercises

21.3 | Calculate the mass defect for the neon-20 nucleus. The mass of neon-20 is 19.992440 u. (*Hint*: How many protons and neutrons does neon-20 have?)

21.4 | Calculate the binding energy per nucleon for the boron-10 nucleus, whose mass is 10.012937 u.

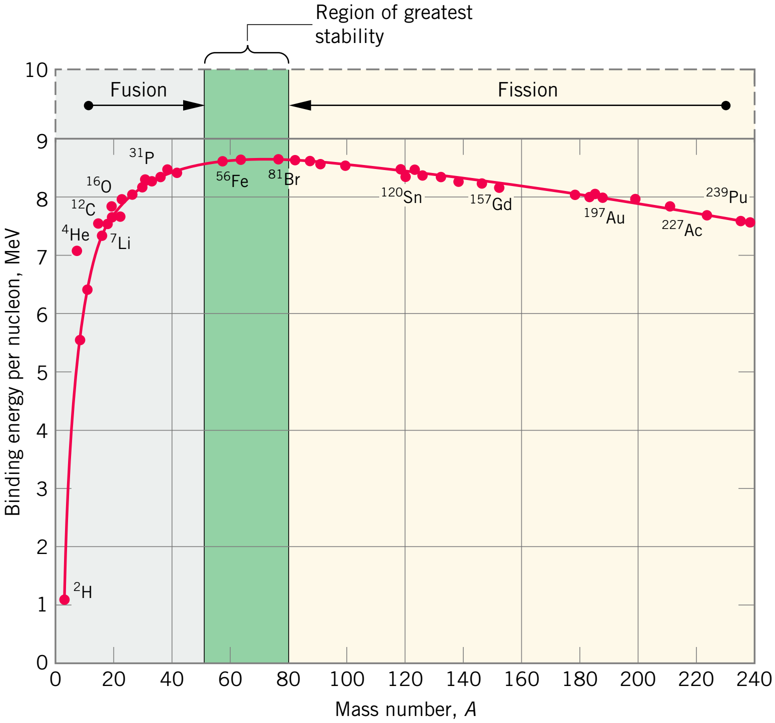


Figure 21.1 | **Binding energies per nucleon.** ES: Can we update this reference since it has been in more recent editions of the book. (*From D. Halliday, R. Resnick, and J. Walker,* Fundamentals of Physics, *9th ed., revised, 2011. John Wiley & Sons, Inc. Used by permission*).

■ Quite often you'll see the terms "atomic fusion" and "atomic fission" used for nuclear fusion and nuclear fission, respectively.

Binding Energy and Nuclear Stability

Figure 21.1 shows a plot of binding energies per nucleon versus mass numbers for most of the elements. We are interested in this because the larger the binding energy per nucleon, the more stable the nucleus. The curve passes through a maximum at iron-56, which means that the iron-56 nuclei are the most stable of all. The plot in Figure 21.1, however, does not have a sharp maximum. Thus, a large number of elements with intermediate mass numbers in the broad center of the periodic table include the most stable isotopes in nature.

Nuclei of low mass number have small binding energies per nucleon. Joining two such nuclei to form a heavier nucleus, a process called **nuclear fusion**, leads to a more stable nucleus and a large increase in binding energy per nucleon. This extra energy is released when the two lighter nuclei fuse (join) and is the origin of the energy released in the cores of stars and the detonation of a hydrogen bomb. Nuclear fusion is discussed further in Section 21.8.

As we follow the plot of Figure 21.1 to the higher mass numbers, the nuclei decrease in stability as the binding energies decrease. Among the heaviest atoms, therefore, we might expect to find isotopes that could change to more stable forms by breaking up into lighter nuclei, by undergoing nuclear fission. **Nuclear fission**, the subject of Section 21.8, is the spontaneous breaking apart of a nucleus to form isotopes of intermediate mass number.

21.3 | Radioactivity

Except for hydrogen, all atomic nuclei have more than one proton, each of which carries a positive charge. Because like charges repel, we might wonder how any nucleus could be stable. However, the electrostatic forces of attraction and repulsion, such as the kinds present among the ions in a crystal of sodium chloride, are not the only forces at work in the nucleus. Protons do, indeed, repel each other electrostatically, but another force, a force of attraction called the *nuclear strong force,* also acts in the nucleus. The nuclear strong force, effective only at very short distances, overcomes the electrostatic force of repulsion between protons, and it binds both protons and neutrons into a nuclear package. Moreover, the neutrons, by helping to keep the protons farther apart, also lessen repulsions between protons.

■ Adjacent neutrons experience no electrostatic repulsion between each other, only the attractive strong force.

One consequence of the difference between the nuclear strong force and the electrostatic force occurs among nuclei that have large numbers of protons but too few intermingled neutrons to dilute the electrostatic repulsions between protons. Such nuclei are often unstable because their nuclei carry excess energy. To achieve a lower energy and thus more stability, unstable nuclei have a tendency to eject small nuclear fragments, and many simultaneously release high-energy electromagnetic radiation. The stream of particles (or photons) coming from the sample is called **nuclear radiation** or **atomic radiation** and the phenomenon is called **radioactivity.** Isotopes that exhibit this property are called **radionuclides.** About 60 of the approximately 350 naturally occurring isotopes are radioactive.

In a sample of a given radionuclide, not all of the atoms undergo change at once. The rate at which radiation is emitted (which translates into the intensity of the radiation) depends on the identity of the isotope in the sample. Over time, as radioactive nuclei change into stable ones, the number of atoms of the radionuclide remaining in the sample decreases, causing the intensity of the radiation to drop, or *decay*. The radionuclide is said to undergo **radioactive decay.**

Naturally occurring atomic radiation consists principally of three kinds: alpha, beta, and gamma radiation, as discussed below. Other types of radiation also occur. They are summarized in Table 21.1 and are described on the pages ahead.

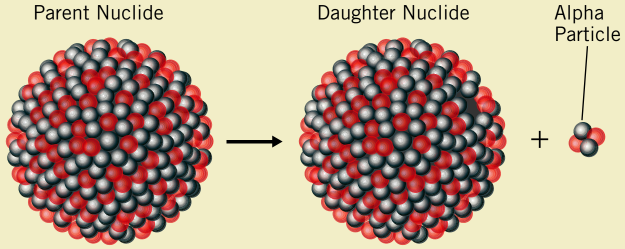
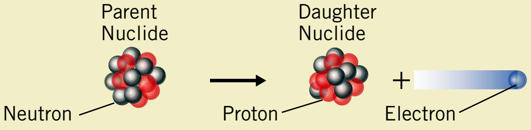
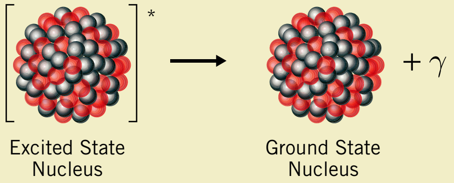
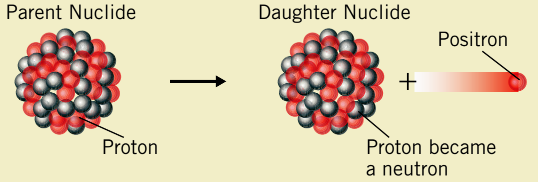
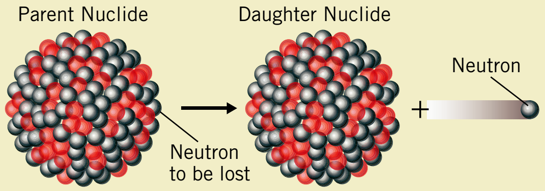
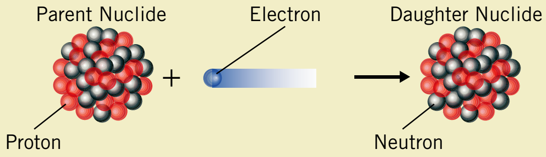
Alpha Radiation

Alpha radiation consists of a stream of helium nuclei called **alpha particles**, symbolized as ${}^{4}_{2}\text{He}$, where 4 is the mass number and 2 is the atomic number. The alpha particle bears a charge of 2+, but the charge is omitted from the symbol.

Alpha particles are the most massive of those commonly emitted by radionuclides. When ejected (Figure 21.2), alpha particles move through the atom's electron orbitals,

■ In Chapter 3 you learned that an isotope is identified by writing its mass number, A, as a superscript and its atomic number, Z, as a subscript in front of the chemical symbol, X, as in ${}^{A}_{Z}X$. We use this same notation in representing particles involved in nuclear reactions. For particles that are not atomic nuclei, Z stands for the charge on the particle.

Table 21.1 Nuclear Reactions

Type of Radioactivity	**Particle**	**Symbol**	**Equation Example**	**Example**
Alpha Radiation	${}^{4}_{2}\text{He}$	${}^{4}_{2}\alpha$	${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\text{He}$ ${}^{263}_{106}\text{Sg} \rightarrow {}^{259}_{104}\text{Rf} + {}^{4}_{2}\text{He}$	 Parent Nuclide Daughter Nuclide Alpha Particle
Beta Radiation	${}^{0}_{-1}e$	${}^{0}_{-1}\beta$	${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + {}^{0}_{-1}e$ ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e$	 Parent Nuclide Daughter Nuclide Neutron Proton Electron
Gamma Radiation	${}^{0}_{0}\gamma$	γ	${}^{A}_{Z}X^{*} \rightarrow {}^{A}_{Z}X + \gamma$ ${}^{60}_{28}\text{Ni}^{*} \rightarrow {}^{60}_{28}\text{Ni} + \gamma$	 * Excited State Nucleus Ground State Nucleus
Positron Emission	${}^{0}_{1}e$	${}^{0}_{+1}\beta$	${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Z + {}^{0}_{1}e$ ${}^{54}_{27}\text{Co} \rightarrow {}^{54}_{26}\text{Fe} + {}^{0}_{1}e$	 Parent Nuclide Daughter Nuclide Positron Proton Proton became a neutron
Neutron Emission	${}^{1}_{0}n$	${}^{1}_{0}n$	${}^{A}_{Z}X \rightarrow {}^{A-1}_{Z}X + {}^{1}_{0}n$ ${}^{87}_{36}\text{Kr} \rightarrow {}^{86}_{36}\text{Kr} + {}^{1}_{0}n$	 Parent Nuclide Daughter Nuclide Neutron Neutron to be lost
Electron Capture	${}^{0}_{-1}e$	${}^{0}_{-1}e$	${}^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}^{A}_{Z-1}Y$ ${}^{50}_{23}V + {}^{0}_{-1}e \rightarrow {}^{50}_{22}\text{Ti}$	 Parent Nuclide Electron Daughter Nuclide Proton Neutron

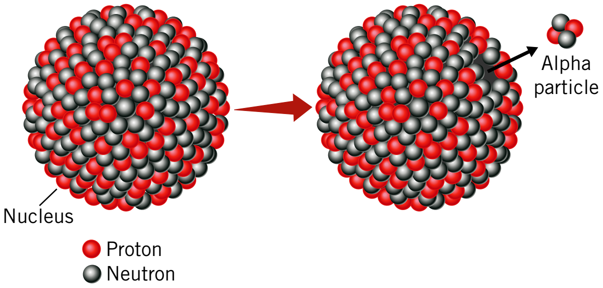


Figure 21.2 | **Emission of an alpha particle from an atomic nucleus.** Removal of $^{4}_{2}\text{He}$ from a nucleus decreases the atomic number by 2 and the mass number by 4.

emerging from the atom at speeds of up to one-tenth the speed of light. Their size, however, prevents them from going far. After traveling at most only a few centimeters in air, alpha particles collide with air molecules, lose kinetic energy, pick up electrons, and become neutral helium atoms. Alpha particles themselves cannot penetrate the skin, although enough exposure causes a severe skin burn. If carried in air or on food into the soft tissues of the lungs or the intestinal tract, emitters of alpha particles can cause serious harm, including cancer.

Nuclear Equations

■ A nuclear transformation such as the alpha decay of ^{238}U does not depend on the chemical environment. The same nuclear equation applies whether the uranium is in the form of the free element or in a compound.

To symbolize the decay of a nucleus, we construct a **nuclear equation**, which we can illustrate by the alpha decay of uranium-238 to thorium-234:

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Unlike chemical reactions, nuclear reactions produce new isotopes, so we need separate rules for balancing nuclear equations.

TOOLS

Balancing nuclear equations

Rules for balancing a nuclear equation:

1. *The sum of the mass numbers on each side of the arrow must be the same.*
2. *The sum of the atomic numbers (nuclear charge) on each side of the arrow must be the same.*

In the nuclear equation for the decay of uranium-238, the atomic numbers balance $(90 + 2 = 92)$, and the mass numbers balance $(234 + 4 = 238)$. Notice that electrical charges are not shown, even though they are there (initially). The alpha particle, for example, has a charge of 2+. If it was emitted by a neutral uranium atom, then the thorium particle initially has a charge of 2−. These charged particles, however, eventually pick up or lose electrons either from each other or from molecules in the matter through which they travel.

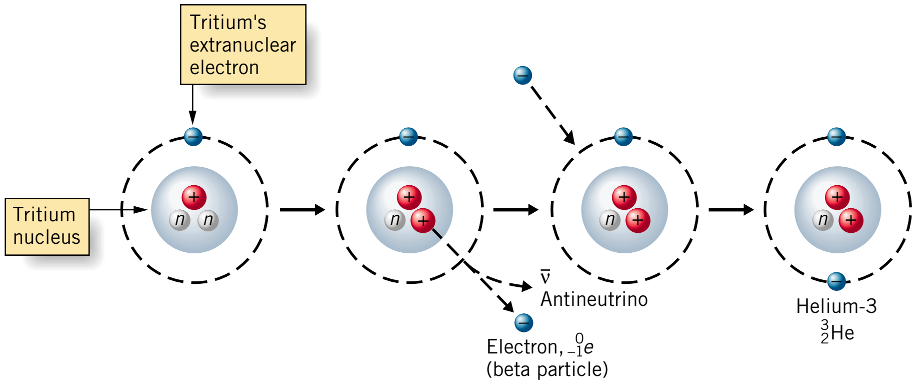
Beta Radiation

Naturally occurring **beta radiation** consists of a stream of electrons, which in this context are called **beta particles**. In a nuclear equation, the beta particle has the symbol $_{-1}^{0}e$, because the electron's mass number is 0 and its charge is 1−. Hydrogen-3 (tritium) is a beta emitter that decays by the following equation:

■ Sometimes the beta particle is given the symbol $_{-1}^{0}\beta$, or simply $\beta-$.

$$\underset{\text{tritium}}{^{3}_{1}\text{H}} \longrightarrow \underset{\text{helium-3}}{^{3}_{2}\text{He}} + \underset{\substack{\text{beta-particle}\\ \text{(electron)}}}{^{0}_{-1}e} + \underset{\text{antineutrino}}{\overline{\nu}}$$

Both the antineutrino (to be described further shortly) and the beta particle come from the atom's nucleus, not its electron shells. We do not think of them as having a prior existence in the nucleus, any more than a photon exists before its emission from an excited



Tritium's extranuclear electron
Tritium nucleus
n n
n
Antineutrino
Electron, ${}^{0}_{-1}e$ (beta particle)
Helium-3
${}^{3}_{2}$He

Figure 21.3 | **Emission of a beta particle from a tritium nucleus.** Emission of a beta particle changes a neutron into a proton. This results in a positively charged ion, which picks up an electron to become a neutral atom.

atom (see Figure 21.3). Both the beta particle and the antineutrino are created during the decay process in which a neutron is transformed into a proton:

$$\underset{\substack{\text{neutron}\\\text{(in the}\\\text{nucleus)}}}{{}^{1}_{0}n} \longrightarrow \underset{\substack{\text{beta particle}\\\text{(emitted)}}}{{}^{0}_{-1}e} + \underset{\substack{\text{proton}\\\text{(remains in}\\\text{the nucleus)}}}{{}^{1}_{1}p} + \underset{\substack{\text{antineutrino}\\\text{(emitted)}}}{\overline{\nu}}$$

Unlike alpha particles, which are all emitted with the same discrete energy from a given radionuclide, beta particles emerge from a given beta emitter with a continuous spectrum of energies. Their energies vary from zero to some characteristic fixed upper limit for each radionuclide. This fact once gave nuclear physicists considerable trouble, partly because it was an apparent violation of energy conservation. To solve this problem, Wolfgang Pauli proposed in 1927 that beta emission is accompanied by emission of yet another decay particle, this one electrically neutral and almost massless. Enrico Fermi suggested the name *neutrino* ("little neutral one"), but eventually it was named the *antineutrino*, symbolized by $\overline{\nu}$.

An electron is extremely small, so a beta particle is less likely to collide with any atoms or molecules in the medium through which it travels. Depending on its initial kinetic energy, a beta particle can travel up to 300 cm (about 10 ft) in dry air, much farther than alpha particles. However, only the highest energy beta particles can penetrate the skin.

Gamma Radiation

■ Gamma photons have the symbol ${}^{0}_{0}\gamma$ because they have no charge or mass.

Gamma radiation, which often accompanies most nuclear decays, consists of high-energy photons given the symbol ${}^{0}_{0}\gamma$ or, often, simply γ in equations. Gamma radiation is extremely penetrating and is effectively blocked only by very dense materials, like lead.

The emission of gamma radiation involves transitions between energy levels *within* the nucleus. Nuclei have energy levels of their own, much as atoms have orbital energy levels. When a nucleus emits an alpha or beta particle, it sometimes is left in an excited energy state. By the emission of a gamma-ray photon, the nucleus relaxes into a more stable state. For example, cobalt-60 emits a beta particle and forms a nickel-60 isotope in a nuclear excited state, which then emits two γ particles.

$${}^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni}^{*} + {}^{0}_{-1}e \longrightarrow {}^{60}_{28}\text{Ni} + 2\gamma$$

The excited state is indicated by an asterisk.

The Electron Volt

The energy carried by a given radiation is usually described by an energy unit new to our study, the **electron volt**, abbreviated **eV**; 1 eV is the energy an electron receives when accelerated under the influence of 1 volt. It is related to the joule as follows:

$$1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$$

As you can see, the electron volt is an extremely small amount of energy, so multiples are commonly used, such as the kilo-, mega-, and gigaelectron volt.

$$1 \text{ keV} = 10^3 \text{ eV}$$
$$1 \text{ MeV} = 10^6 \text{ eV}$$
$$1 \text{ GeV} = 10^9 \text{ eV}$$

An alpha particle emitted by radium-224 has an energy of 5 MeV. Hydrogen-3 (tritium) emits beta radiation at an energy of 0.05 to 1 MeV. The gamma radiation from cobalt-60, the radiation currently used to kill bacteria and other pests in certain foods, consists of photons with energies of 1.173 MeV and 1.332 MeV.

In the interconversion of mass and energy,

$$1 \text{ eV} \Leftrightarrow 1.783 \times 10^{-36} \text{ kg}$$
$$1 \text{ MeV} \Leftrightarrow 1.78 \times 10^{-27} \text{ g}$$
$$1 \text{ GeV} \Leftrightarrow 1.783 \times 10^{-24} \text{ g}$$

Example 21.1
Writing a Balanced Nuclear Equation

Cesium-137, $^{137}_{55}\text{Cs}$, one of the radioactive wastes from a nuclear power plant or an atomic bomb explosion, emits beta and gamma radiation. Write the nuclear equation for the decay of cesium-137.

Ions of cesium, which is in the same family as sodium, travel in the body to many of the same sites where sodium ions go.

Analysis: We are being asked to balance a nuclear equation, and when we do this, we need to keep track of the atomic numbers and the mass numbers.

Assembling the Tools: We will start with an incomplete equation using the given information. Then we will use the requirements for a balanced nuclear equation as a tool to figure out any other data needed to complete the equation. We also have to realize that a beta particle is an electron emitted from the nucleus as a neutron is converted into a proton and an electron, and its symbol is ${}^{0}_{-1}e$. Therefore, the atomic number will have to go up by one.

Solution: The incomplete nuclear equation is

$$^{137}_{55}\text{Cs} \longrightarrow {}^{0}_{-1}e + {}^{0}_{0}\gamma + {}^{\overset{\text{Mass number goes here.}}{\underline{\qquad}}}_{\underset{\text{Atomic number goes here.}}{\underline{\qquad}}}\underset{\text{Atomic symbol goes here.}}{\underline{\qquad}}$$

After we have determined the atomic number, Z, the atomic symbol can be obtained from the periodic table. Z is found using the fact that the atomic number (55) on the left side of the equation must equal the sum of the atomic numbers on the right side.

$$55 = -1 + 0 + Z$$
$$Z = 56$$

According to the periodic table, element 56 is Ba (barium). To determine which isotope of barium forms, we use the requirement that the sums of the mass numbers on either side of the equation must also be equal. Letting A be the mass number of the barium isotope,

$$137 = 0 + 0 + A$$
$$A = 137$$

The balanced nuclear equation, therefore, is

$$^{137}_{55}\text{Cs} \longrightarrow {}^{0}_{-1}e + {}^{0}_{0}\gamma + {}^{137}_{56}\text{Ba}$$

■ **Is the Answer Reasonable?** Besides double-checking that element 56 is barium, the answer satisfies the requirements of a nuclear equation—namely, the sums of the mass numbers, 137, are the same on both sides, as are the sums of the atomic numbers.

Practice Exercises

21.5 | Marie Curie earned one of her two Nobel Prizes for isolating the element radium, which soon became widely used to treat cancer. Radium-226, ${}^{226}_{88}\text{Ra}$, emits a gamma photon plus an alpha particle to give radon-222. Write a balanced nuclear equation for its decay and identify the particle that's emitted. (*Hint*: Be sure to balance atomic numbers and mass numbers.)

21.6 | Write the balanced nuclear equation for the decay of strontium-90, a beta emitter. (Strontium-90 is one of the many radionuclides present in the wastes of operating nuclear power plants.)

Positron and Neutron Emission

Many *synthetic isotopes* (isotopes not found in nature, but synthesized by methods discussed in Section 21.5) emit *positrons*, which are particles with the mass of an electron but a positive instead of a negative charge. A **positron** is a positive beta particle, a positive electron, and its symbol is ${}^{0}_{1}e$. It forms in the nucleus by the conversion of a proton to a neutron (Figure 21.4). Positron emission, like beta emission, is accompanied by a chargeless and virtually massless particle, a *neutrino* (ν), the counterpart of the antineutrino ($\overline{\nu}$) in the realm of *antimatter* (defined below). Cobalt-54, for example, is a positron emitter and changes to a stable isotope of iron:

■ The symbol ${}^{+}\beta$ is sometimes used for the positron.

$$ {}^{54}_{27}\text{Co} \longrightarrow {}^{54}_{26}\text{Fe} + \underset{\text{positron}}{{}^{0}_{1}e} + \underset{\text{neutrino}}{\nu} $$

A positron, when emitted, eventually collides with an electron, and the two annihilate each other (Figure 21.5). Their masses change entirely into the energy of two gamma-ray photons called *annihilation radiation photons*, each with an energy of 511 keV.

$$ {}^{0}_{-1}e + {}^{0}_{1}e \longrightarrow 2\,{}^{0}_{0}\gamma $$

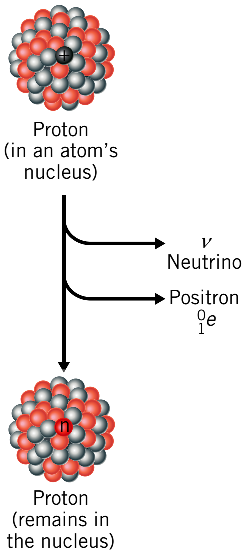


Figure 21.4 | **The emission of a positron replaces a proton by a neutron.**

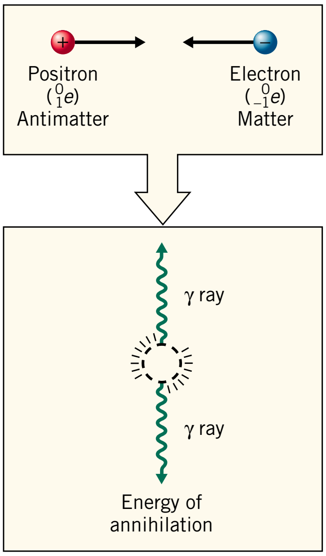


Figure 21.5 | **Gamma radiation is produced when a positron and an electron collide.** The annihilation of a positron and an electron leads to two gamma ray photons that go in exactly opposite directions.

Because a positron destroys a particle of ordinary matter (an electron), it is called a particle of antimatter. To be classified as **antimatter**, a particle must have a counterpart among one of ordinary matter, and the two must annihilate each other when they collide. For example, a neutron and an antineutron represent such a pair and annihilate each other when they come in contact.

Neutron emission, another kind of nuclear reaction, leads to a different isotope of the same element. Neutron emission occurs when an isotope has an excess of neutrons. Krypton-87, for example, decays as follows to krypton-86:

$$^{87}_{36}\mathrm{Kr} \longrightarrow {}^{86}_{36}\mathrm{Kr} + \underset{\text{neutron}}{{}^{1}_{0}n}$$

X-rays and Electron Capture

■ X rays used in diagnosis typically have energies of 100 keV or less.

X rays, like gamma rays, consist of high-energy electromagnetic radiation, but their energies are usually less than those of gamma radiation. Although X rays are emitted by some synthetic radionuclides, when needed for medical diagnostic work they are generated by focusing a high-energy electron beam onto a metal target.

Electron capture, yet another kind of nuclear reaction, is very rare among natural isotopes but common among synthetic radionuclides. For example, an electron can be captured from the orbital electron shell having $n = 1$ or $n = 2$ by a vanadium-50 nucleus, causing it to change to a stable ^{50}Ti nucleus. The transformation is accompanied by the emission of X rays and a neutrino.

$$^{50}_{23}\mathrm{V} + {}^{0}_{-1}e \xrightarrow{\text{Electron capture}} {}^{50}_{22}\mathrm{Ti} + \text{X rays} + v$$

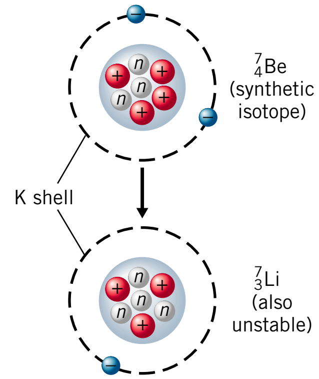

$^{7}_{4}$Be (synthetic isotope)
K shell
$^{7}_{3}$Li (also unstable)
n
+

Figure 21.6 | **Electron capture.** Electron capture is the collapse of an orbital electron into the nucleus, and this changes a proton into a neutron. A gap is left in a low-energy electron orbital. When an electron drops from a higher orbital to fill the gap, an X-ray photon is emitted.

The net effect in the nucleus of electron capture is the conversion of a proton into a neutron (Figure 21.6):

$$\underset{\substack{\text{proton}\\ \text{(in the nucleus)}}}{{}^{1}_{1}p} + \underset{\substack{\text{electron (captured}\\ \text{from the 1}s\text{ orbital)}}}{{}^{0}_{-1}e} \longrightarrow \underset{\substack{\text{neutron}\\ \text{(in the nucleus)}}}{{}^{1}_{0}n}$$

Electron capture does not change an atom's mass number, only its atomic number. It also leaves a hole in the first or second electron shell, and the atom emits photons of X rays as other orbital electrons drop down to fill the hole. Moreover, the nucleus that has just captured an orbital electron may be in an excited energy state and so can emit a gamma-ray photon.

Radioactive Disintegration Series

Sometimes a radionuclide does not decay directly to a stable isotope, but decays instead to another unstable radionuclide. The decay of one radionuclide after another will continue until a stable isotope forms. The sequence of such successive nuclear reactions is called a **radioactive disintegration series.** Four such series occur naturally. Uranium-238 is at the head of one of them (Figure 21.7).

The rates of decay of radionuclides vary and are usually described by specifying their half-lives, $t_{1/2}$, a topic we studied in Section 14.4. One *half-life* period in nuclear science is the time it takes for a given sample of a radionuclide to decay to one-half of its initial amount. Radioactive decay is a first-order process, so the period of time taken by one half-life is independent of the initial number of nuclei. The huge variations in the half-lives of several radionuclides are shown in Table 21.2.

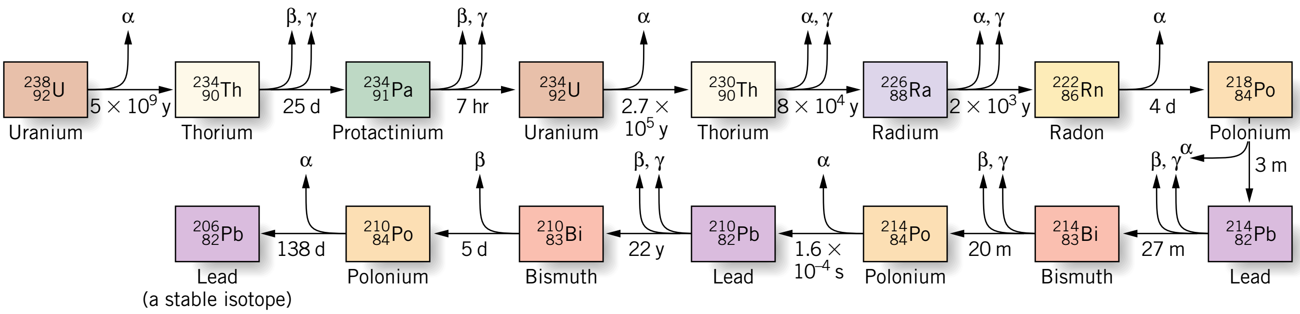

$^{238}_{92}$U
Uranium
α
5 × 10^9 y
$^{234}_{90}$Th
Thorium
β, γ
25 d
$^{234}_{91}$Pa
Protactinium
β, γ
7 hr
$^{234}_{92}$U
Uranium
α
2.7 × 10^5 y
$^{230}_{90}$Th
Thorium
α, γ
8 × 10^4 y
$^{226}_{88}$Ra
Radium
α, γ
2 × 10^3 y
$^{222}_{86}$Rn
Radon
α
4 d
$^{218}_{84}$Po
Polonium
α
3 m
$^{214}_{82}$Pb
Lead
β, γ
27 m
$^{214}_{83}$Bi
Bismuth
β, γ
20 m
$^{214}_{84}$Po
Polonium
α
1.6 × 10^{-4} s
$^{210}_{82}$Pb
Lead
β, γ
22 y
$^{210}_{83}$Bi
Bismuth
β
5 d
$^{210}_{84}$Po
Polonium
α
138 d
$^{206}_{82}$Pb
Lead
(a stable isotope)

Figure 21.7 | **The uranium-238 radioactive disintegration series.** The time given beneath each arrow is the half-life period of the preceding isotope (y = year, m = month, d = day, hr = hour, mi = minute, and s = second).

Table 21.2 **Typical Half-Life Periods**

Element	Isotope	Half-life	Radiations or Mode of Decay
Naturally occurring radionuclides			
Potassium	$^{40}_{19}$K	1.3 × 10^9 yr	beta, gamma
Tellurium	$^{123}_{52}$Te	1.2 × 10^{13} yr	electron capture
Neodymium	$^{144}_{60}$Nd	5 × 10^{15} yr	alpha
Samarium	$^{149}_{62}$Sm	4 × 10^{14} yr	alpha
Rhenium	$^{187}_{75}$Re	7 × 10^{10} yr	beta
Radon	$^{222}_{86}$Rn	3.82 day	alpha
Radium	$^{226}_{88}$Ra	1590 yr	alpha, gamma
Thorium	$^{230}_{90}$Th	8 × 10^4 yr	alpha, gamma
Uranium	$^{238}_{92}$U	4.51 × 10^9 yr	alpha
Synthetic radionuclides			
Tritium	$^{3}_{1}$H($^{3}_{1}$T)	12.26 yr	beta
Oxygen	$^{15}_{8}$O	124 s	positron
Phosphorus	$^{32}_{15}$P	14.3 day	beta
Technetium	$^{99m}_{43}$Tc	6.02 hr	gamma
Iodine	$^{131}_{53}$I	8.07 day	beta
Cesium	$^{137}_{55}$Cs	30.1 yr	beta
Strontium	$^{90}_{38}$Sr	28.1 yr	beta
Plutonium	$^{238}_{94}$Pu	87.8 yr	alpha
Americium	$^{243}_{95}$Am	7.37 × 10^3 yr	alpha

Practice Exercises

21.7 | Carbon-11 is an isotope with a neutron-poor nucleus and is a positron emitter. Write the balanced nuclear equation for the decay of carbon-11. (*Hint*: What nuclide is formed when a positron is emitted?)

21.8 | Beryllium-13 is neutron rich and is a neutron emitter. Write the balanced nuclear equation for the decay of beryllium-13.

21.9 | Selenium-72 decays to arsenic-72 by electron capture, which in turn is used for PET imaging. Write a balanced nuclear equation for the decay of selenium-72.

21.4 | Band of Stability

Figure 21.8 plots all of the known isotopes of all of the elements, both stable and unstable, according to their numbers of protons and neutrons. The two curved lines in Figure 21.8 enclose a zone, called the **band of stability**, within which lie all stable nuclei. (No isotope above element 83, bismuth, is included in Figure 21.8 because none has a *stable* isotope.) Within the band of stability are also some unstable isotopes, because smooth lines cannot be drawn to exclude them.

Any isotope not represented anywhere on the array, inside or outside the band of stability, probably has a half-life too short to permit its detection. For example, an isotope with 50 neutrons and 60 protons would lie well below the band of stability and would likely be

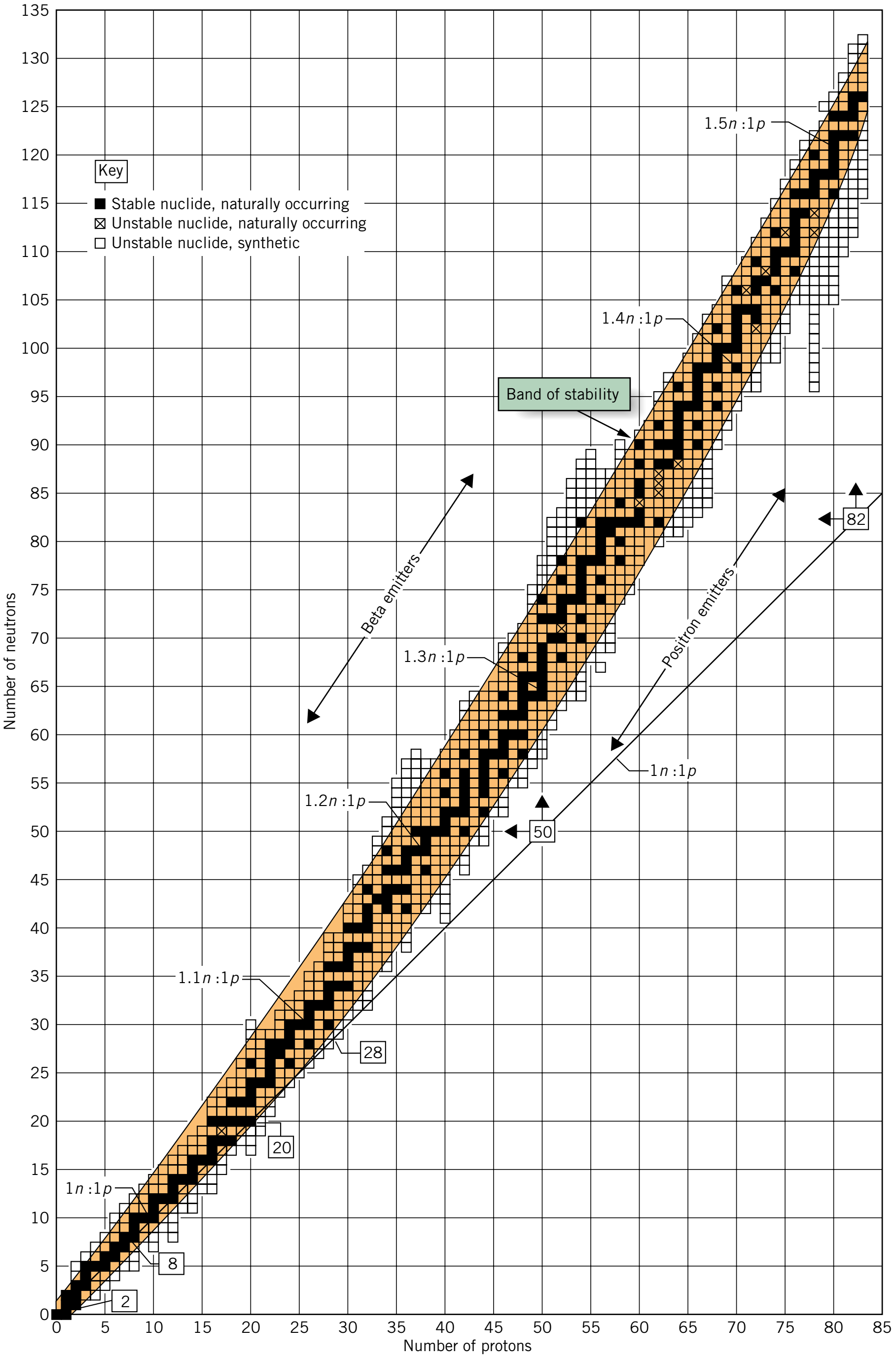


Figure 21.8 | **The band of stability.** Stable nuclei fall within a narrow band in a plot of the number of neutrons versus the number of protons. Nuclei far outside the band are too unstable to exist.

extremely unstable. Any attempt to synthesize it would likely be a waste of time and money.

Notice that the band curves slightly upward as the number of protons increases. The curvature means that the *ratio* of neutrons to protons gradually increases from 1:1, a ratio indicated by the straight line in Figure 21.8. This occurs because more protons require more neutrons to provide a compensating nuclear strong force and to dilute electrostatic proton–proton repulsions.

Nuclear Reactions of Unstable Nuclei

The isotopes with atomic numbers above 83 tend to be alpha emitters. Isotopes occurring above and to the left of the band of stability tend to be beta emitters. Isotopes lying below and to the right of the band are positron emitters. Are there any reasons for these tendencies?

Alpha Emitters

The alpha emitters, as we said, occur mostly among the radionuclides above atomic number 83. Their nuclei have too many protons, and the most efficient way to lose protons is by the loss of an alpha particle.

Beta Emitters

Beta emitters are generally above the band of stability and so have neutron-to-proton ratios that evidently are too high. By beta decay, a nucleus loses a neutron and gains a proton, thus decreasing the ratio:

$$^1_0n \longrightarrow {}^1_1p + {}^0_{-1}e + \overline{\nu}$$

■ The proton can also be given the symbol $^1_1$H in nuclear equations.

For example, by beta decay, fluorine-20 decreases its neutron-to-proton ratio from 11/9 to 10/10:

$$^{20}_{9}\text{F} \longrightarrow {}^{20}_{10}\text{Ne} + {}^0_{-1}e + \overline{\nu}$$

$$\frac{\text{neutron}}{\text{proton}} = \frac{11}{9} \longrightarrow \frac{10}{10}$$

The surviving nucleus, neon-10, is closer to the center of the band of stability. Figure 21.9, an enlargement of the fluorine part of Figure 21.8, explains this change

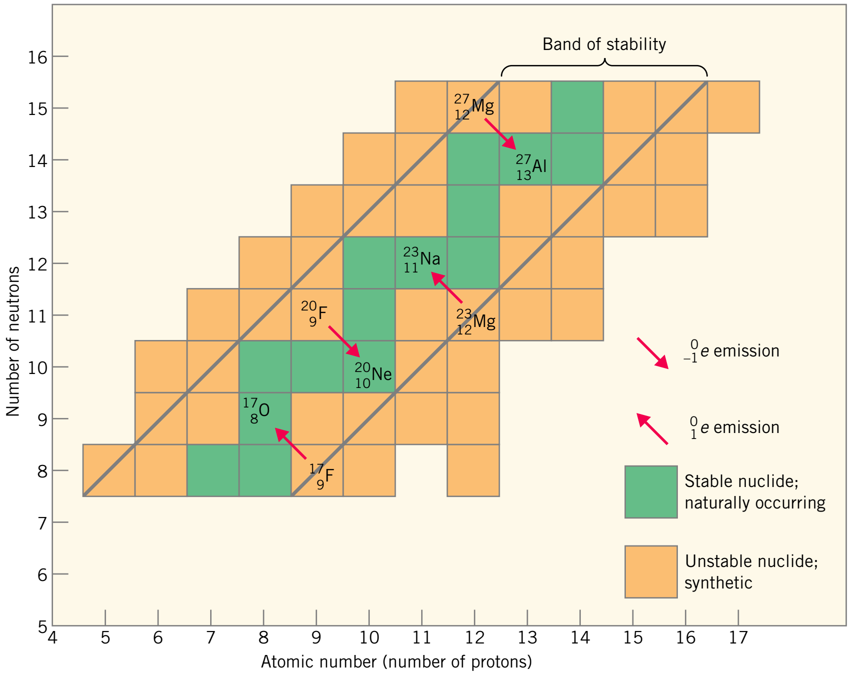


Figure 21.9 | **An enlarged section of the band of stability.** Beta decay from magnesium-27 and fluorine-20 reduces their neutron-to-proton ratio and moves them closer to the band of stability. Positron decay from magnesium-23 and fluorine-17 increases this ratio and moves these nuclides closer to the band of stability, too.

further. Figure 21.9 also shows how the beta decay of magnesium-27 to aluminum-27 lowers the neutron-to-proton ratio.

Positron Emitters

In nuclei with too few neutrons to be stable, positron emission increases the neutron-to-proton ratio by changing a proton into a neutron. A fluorine-17 nucleus, for example, increases its neutron-to-proton ratio, improves its stability, and moves into the band of stability by emitting a positron and a neutrino and changing to oxygen-17 (see Figure 21.9):

$$^{17}_{9}\mathrm{F} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{0}_{1}e + v$$

$$\frac{\text{neutron}}{\text{proton}} = \frac{8}{9} \longrightarrow \frac{9}{8}$$

Positron decay by magnesium-23 to sodium-23 produces a similarly favorable shift (also shown in Figure 21.9).

Odd–Even Rule

Study of the compositions of stable nuclei reveals that nature favors even numbers for protons and neutrons. This is summarized by the **odd–even rule**.

TOOLS

Odd–even rule

Odd–Even Rule

When the numbers of neutrons and protons in a nucleus are both even, the isotope is far more likely to be stable than when both numbers are odd.

CHEMISTRY ON THE CUTTING EDGE 21.1

Positron Emission Tomography (PET)

Positron emitters are used in an important method for studying brain function called the PET scan, for *positron emission tomography*. The technique begins by chemically incorporating positron-emitting radionuclides into molecules, like glucose, that can be absorbed by the brain directly from the blood. It's like inserting radiation generators that act from within the brain rather than focusing X rays or gamma rays from the outside. Carbon-11, for example, is a positron emitter whose atoms can be used in place of carbon-12 atoms in glucose molecules, $C_6H_{12}O_6$. (One way to prepare such glucose is to let a leafy vegetable, Swiss chard, use $^{11}CO_2$ to make the glucose by photosynthesis.)

A PET scan using tiny amounts of carbon-11 glucose detects situations where glucose is not taken up normally—for example, in manic depression, schizophrenia, and Alzheimer's disease. After the carbon-11 glucose is ingested by the patient, radiation detectors outside the body pick up the annihilation radiation produced when electrons react with positrons emitted at specifically those brain sites that use glucose. These positrons emit gamma rays in opposite directions. When the pairs of gamma rays are detected 180 degrees apart, the acquisition time can be used to back calculate exactly where the radiation came from. By mapping the locations of the brain sites using the tagged glucose, a picture showing brain function can be formed. PET scan technology, for example, demonstrated that the uptake of glucose by the brains of smokers is less than that of nonsmokers, as shown in Figure 1.

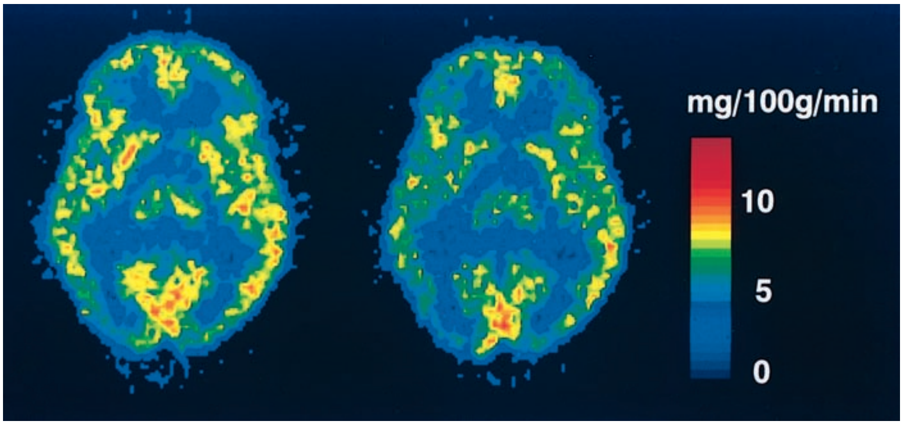


Figure 1 **Positron emission tomography (PET) in the study of brain activity.** (Left) Nonsmoker. (Right) Smoker. The PET scan reveals widespread reduction in the rate of glucose metabolism when nicotine is present. *(Courtesy of E. D. London, National Institute on Drug Abuse)*

Of the 264 stable isotopes, only five have odd numbers of both protons and neutrons, whereas 157 have even numbers of both. The rest have an odd number of one nucleon and an even number of the other. To see this, notice in Figure 21.8 how the horizontal lines with the largest numbers of dark squares (stable isotopes) most commonly correspond to even numbers of neutrons. Similarly, the vertical lines with the most dark squares most often correspond to even numbers of protons.

■ These five stable isotopes, $^{2}_{1}\text{H}$, $^{6}_{3}\text{Li}$, $^{10}_{5}\text{B}$, $^{14}_{7}\text{N}$, and $^{138}_{57}\text{La}$, all have odd numbers of both protons and neutrons.

The odd–even rule is related to the spins of nucleons. Both protons and neutrons behave as though they spin like orbital electrons. When two protons or two neutrons have paired spins, meaning the spins are opposite, their combined energy is less than when the spins are unpaired. Only when there are even numbers of protons and neutrons can all of the spins be paired and so give the nucleus a lower energy and greater stability. The least stable nuclei tend to be those with both an odd number of protons and an odd number of neutrons.

Nuclear Magic Numbers

Another rule of thumb for nuclear stability is based on *magic numbers* of nucleons. Isotopes with specific numbers of protons or neutrons, the **magic numbers,** are more stable than the rest. The magic numbers of nucleons are 2, 8, 20, 28, 50, 82, and 126, and where they fall is shown in Figure 21.8 (except for magic number 126).

When the numbers of both protons and neutrons are the same magic number, as they are in $^{4}_{2}\text{He}$, $^{16}_{8}\text{O}$, and $^{40}_{20}\text{Ca}$, the isotope is very stable. $^{100}_{50}\text{Sn}$ also has two identical magic numbers. Although this isotope of tin is unstable, having a half-life of only several seconds, it is much more stable than nearby radionuclides, whose half-lives are in milliseconds. Thus, although tin-100 lies well outside the band of stability, it is stable enough to be observed. One stable isotope of lead, $^{208}_{82}\text{Pb}$, involves two different magic numbers—namely, 82 protons and 126 neutrons.

■ Magic numbers do not cancel the need for a favorable neutron/proton ratio. An atom with 82 protons and 82 neutrons lies far outside the band of stability, and yet 82 is a magic number.

The existence of magic numbers supports the hypothesis that a nucleus has a shell structure with energy levels analogous to electron energy levels. Electron levels, as you already know, are associated with their own special numbers, those that equal the maximum number of electrons allowed in a principal energy level: 2, 8, 18, 32, 50, 72, and 98 (for principal levels with n equal to 1, 2, 3, 4, 5, 6, and 7, respectively). The total numbers of electrons in the atoms of the most chemically stable elements—the noble gases—also make up a special set: 2, 10, 18, 36, 54, and 86 electrons. Thus, special sets of numbers are not unique to nuclei.

Practice Exercises

21.10 | Curium-242 has 96 protons and 146 neutrons. What is the most probable form of radioactive decay for Cm-242? (*Hint*: Where would Cm-242 be found relative to the band of stability in Figure 21.8?)

21.11 | What is the most probable radioactive decay route for the iron-59 isotope of iron?

21.5 | Transmutation

The change of one isotope into another is called **transmutation**, and radioactive decay is only one cause. Transmutation can also be forced by the bombardment of nuclei with high-energy particles, such as alpha particles from natural emitters, neutrons from atomic reactors, or protons made by stripping electrons from hydrogen. To make them better bombarding missiles, protons and alpha particles can be accelerated in an electrical field (Figure 21.10). This gives them greater energy and enables them to sweep through the target atom's orbital electrons and become buried in its nucleus. Although beta particles can also be accelerated, they are repelled by a target atom's own electrons.

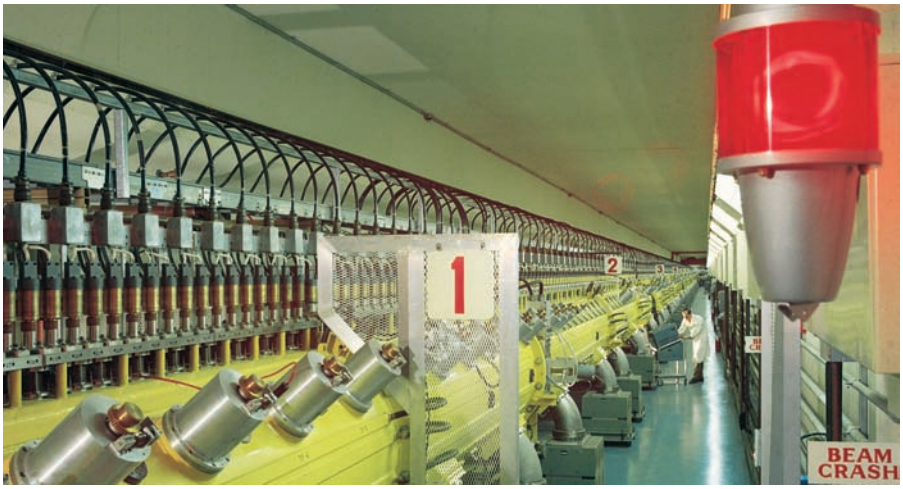


Figure 21.10 | **Linear accelerator.** In this linear accelerator at Brookhaven National Laboratory on Long Island, New York, protons can be accelerated to just under the speed of light and given up to 33 GeV of energy before they strike their target. (1 GeV = 10^9 eV) *(Courtesy Brookhaven National Laboratory)*

Compound Nuclei

■ *Compound* here refers only to the idea of *combination*, not to a chemical.

Both the energy and the mass of a bombarding particle enter the target nucleus at the moment of capture. The new nucleus, called a **compound nucleus**, has excess energy that quickly becomes distributed among all of the nucleons, but the nucleus is nevertheless rendered somewhat unstable. To get rid of the excess energy, a compound nucleus generally ejects something (e.g., a neutron, proton, or electron) and often emits gamma radiation as well. This leaves a new nucleus of an isotope different from the original target, so a transmutation has occurred overall.

Ernest Rutherford observed the first example of artificial transmutation. When he let alpha particles pass through a chamber containing nitrogen atoms, an entirely new radiation was generated, one much more penetrating than alpha radiation. It proved to be a stream of protons (Figure 21.11). Rutherford was able to show that the protons came from the decay of the compound nuclei of fluorine-18, produced when nitrogen-14 nuclei captured bombarding alpha particles:

■ The asterisk, *, symbolizes a high-energy nucleus—a *compound nucleus.*

$$\underset{\text{alpha particle}}{{}^{4}_{2}\text{He}} + \underset{\text{nitrogen nucleus}}{{}^{14}_{7}\text{N}} \longrightarrow \underset{\text{fluorine (compound nucleus)}}{{}^{18}_{9}\text{F}^*} \longrightarrow \underset{\text{oxygen (a rare but stable isotope)}}{{}^{17}_{8}\text{O}} + \underset{\text{proton (high-energy)}}{{}^{1}_{1}p}$$

Another example is the synthesis of alpha particles from lithium-7, in which protons are used as bombarding particles. The resulting compound nucleus, beryllium-8, splits in two.

$$\underset{\text{proton}}{{}^{1}_{1}p} + \underset{\text{lithium}}{{}^{7}_{3}\text{Li}} \longrightarrow \underset{\text{beryllium}}{{}^{8}_{4}\text{Be}^*} \longrightarrow \underset{\text{alpha particles}}{2\,{}^{4}_{2}\text{He}}$$

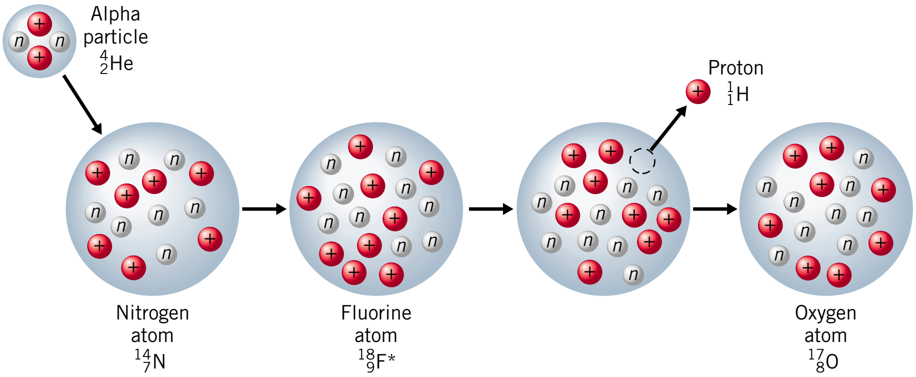

Alpha particle $^{4}_{2}$He
Proton $^{1}_{1}$H
Nitrogen atom $^{14}_{7}$N
Fluorine atom $^{18}_{9}$F*
Oxygen atom $^{17}_{8}$O
n
+

Figure 21.11 | **Transmutation of nitrogen into oxygen.** When the nucleus of nitrogen-14 captures an alpha particle, it becomes a compound nucleus of fluorine-18. This then expels a proton and becomes the nucleus of oxygen-17.

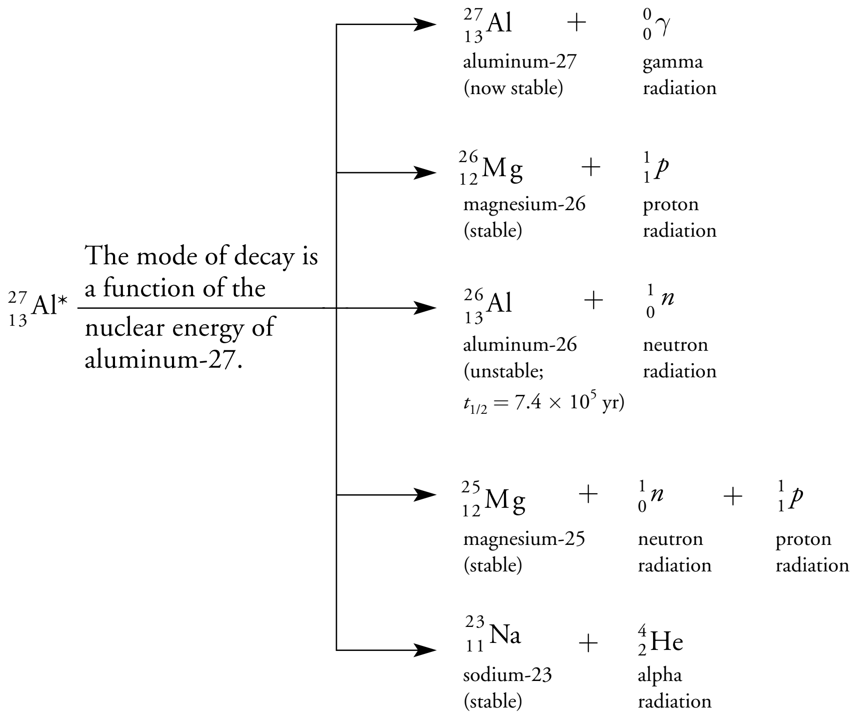
Modes of Decay

A given compound nucleus can be made in a variety of ways. Aluminum-27, for example, forms by any of the following routes:

$$
\begin{aligned}
{}^{4}_{2}\mathrm{He} + {}^{23}_{11}\mathrm{Na} &\longrightarrow {}^{27}_{13}\mathrm{Al}^{*} \\
{}^{1}_{1}p + {}^{26}_{12}\mathrm{Mg} &\longrightarrow {}^{27}_{13}\mathrm{Al}^{*} \\
{}^{2}_{1}\mathrm{H} + {}^{25}_{12}\mathrm{Mg} &\longrightarrow {}^{27}_{13}\mathrm{Al}^{*}
\end{aligned}
$$

■ ${}^{2}_{1}\mathrm{H}$ is a deuteron. It is the nucleus of a deuterium atom, just as a proton is the nucleus of a hydrogen (protium) atom.

Each path gives the compound nucleus ${}^{27}_{13}\mathrm{Al}^{*}$ a different amount of energy. Depending on this energy, different paths of decay are available, and all of the following routes have been observed. They illustrate how the synthesis of such a large number of synthetic isotopes, some stable and others unstable, has been possible.



${}^{27}_{13}\mathrm{Al}^{*}$
The mode of decay is a function of the nuclear energy of aluminum-27.
${}^{27}_{13}\mathrm{Al}$ + ${}^{0}_{0}\gamma$
aluminum-27 (now stable)
gamma radiation
${}^{26}_{12}\mathrm{Mg}$ + ${}^{1}_{1}p$
magnesium-26 (stable)
proton radiation
${}^{26}_{13}\mathrm{Al}$ + ${}^{1}_{0}n$
aluminum-26 (unstable; $t_{1/2} = 7.4 \times 10^{5}$ yr)
neutron radiation
${}^{25}_{12}\mathrm{Mg}$ + ${}^{1}_{0}n$ + ${}^{1}_{1}p$
magnesium-25 (stable)
neutron radiation
proton radiation
${}^{23}_{11}\mathrm{Na}$ + ${}^{4}_{2}\mathrm{He}$
sodium-23 (stable)
alpha radiation

Synthetic Elements

Over a thousand isotopes have been made by transmutations. Most, nearly 900 in number, do not occur naturally; they appear in the band of stability (Figure 21.8) as open squares. The naturally occurring radioactive isotopes above atomic number 83 all have very long half-lives. Others might have existed, but their half-lives probably were too short to permit them to last into our era. All of the elements beyond neptunium (atomic number 93 and higher, known as the **transuranium elements**) are synthetic. Elements from atomic numbers 93 to 103 complete the actinide series of the periodic table, which starts with element 90 (thorium). Beyond this series, elements 104 through 118 have also been made.

To make the heaviest elements, bombarding particles larger than neutrons are used, such as alpha particles or the nuclei of heavier atoms. For example, element 110—darmstadtium, Ds—was made from the compound nucleus formed by the fusion of nickel-62 and lead-208. Darmstadtium-270 decayed to darmstadtium-269 when a neutron was ejected:

■ Element 110 was named after the place of its discovery, Darmstadt, Germany. Element 111 was named in honor of Wilhelm Roentgen, who discovered X rays in 1895.

$${}^{62}_{28}\mathrm{Ni} + {}^{208}_{82}\mathrm{Pb} \longrightarrow {}^{270}_{110}\mathrm{Ds} \longrightarrow {}^{269}_{110}\mathrm{Ds} + {}^{1}_{0}n$$

Similarly, some atoms of element 111 (roentgenium, Rg) formed when a neutron was lost from the compound nucleus made by bombarding bismuth-209 with nickel-64. Most of these heavy atoms are extremely unstable, with half-lives measured in fractions of milliseconds. An exception is element 114; two isotopes have been detected with half-lives reported to be in the tens of seconds.

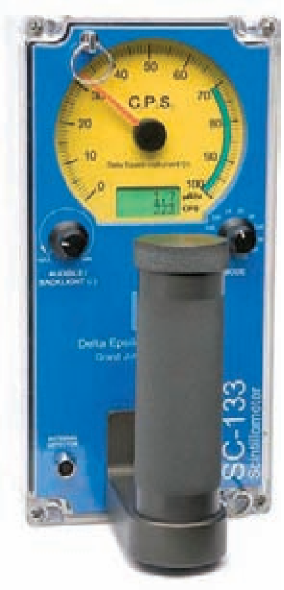


Figure 21.12 | **Scintillation probe.** Energy received from radiations striking the phosphor at the end of this probe is processed by the photomultiplier unit and the counts are measured on the dial. *(Delta Epsilon Instruments, Inc.)*

21.6 | Measuring Radioactivity

Atomic radiation is often described as **ionizing radiation** because it creates ions by knocking electrons from molecules in the matter through which the radiation travels. The generation of ions is behind some of the devices for detecting radiation.

The Geiger–Müller tube, one part of a **Geiger counter**, detects beta and gamma radiation having energy high enough to penetrate the tube's window. Inside the tube is a gas under low pressure in which ions form when radiation enters. The ions permit a pulse of electricity to flow, which activates a current amplifier, a pulse counter, and an audible click.

A **scintillation counter** (Figure 21.12) contains a sensor composed of a substance called a *phosphor* that emits a tiny flash of light when struck by a particle of ionizing radiation. These flashes can be magnified electronically and automatically counted.

The darkening of a photographic film exposed to radiation over a period of time is proportional to the total quantity of radiation received. **Film dosimeters** work on this principle (Figure 21.13), and people who work near radiation sources use them. Each person keeps a log of total exposure, and if a predetermined limit is exceeded, the worker must be reassigned to an unexposed workplace.

Units of Radiation

■ The becquerel is named after Henri Becquerel (1852–1908), the discoverer of radioactivity, who won a Nobel Prize in 1903.

The **activity** of a radioactive material is the number of disintegrations per second. The SI unit of activity is the **becquerel (Bq)**, and it equals one disintegration per second. For example, a liter of air has an activity of about 0.04 Bq, due to the carbon-14 in its carbon dioxide. A gram of natural uranium has an activity of about 2.6×10^4 Bq.

The **curie (Ci)**, named after Marie Curie, who discovered radium, is an older unit, being equal to the activity of a 1.0 g sample of radium-226:

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ disintegrations s}^{-1} = 3.7 \times 10^{10} \text{ Bq} \qquad (21.3)$$

Marie Curie (1867–1934); Nobel Prizes 1903 (physics) and 1911 (chemistry) *(Courtesy College of Physicians of Philadelphia)*

Figure 21.13 | **Badge dosimeter.** *(Cliff Moore/Photo Researchers, Inc.)*

For a sufficiently large sample of a radioactive material, the activity is experimentally found to be proportional to the number of radioactive nuclei, N:

$$\text{activity} = k\,N$$

■ In this discussion, a *disintegration* refers to a single nuclear change that results in the emission of a burst of radiation, which could consist of an alpha particle, beta particle, or gamma photon.

The constant of proportionality, k, is called the **decay constant**. The decay constant is characteristic of the particular radioactive nuclide, and it gives the activity per nuclide in the sample. Since activity is the number of disintegrations per second, and therefore the change in the number of nuclei per second, we can write

$$\text{activity} = -\frac{\Delta N}{\Delta t} = k\,N \tag{21.4}$$

TOOLS Law of radioactive decay

which is called the **law of radioactive decay**.[1] The law shows that radioactive decay is a first-order kinetic process, and the decay constant is really just a first-order rate constant in terms of number of nuclei, rather than concentrations.

Recall from Chapter 14 that the half-life of a first-order reaction is given by Equation 14.7:

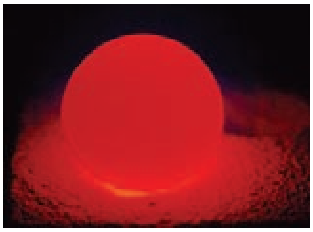
$$t_{1/2} = \frac{\ln 2}{k}$$

TOOLS Half-life of a radionuclide

If we know the half-life of a radioisotope, we can use this relationship to compute its decay constant and also the activity of a known mass of the radioisotope, as Example 21.2 demonstrates.

Example 21.2
Using the Law of Radioactive Decay

Deep-space probes such as NASA's Cassini spacecraft need to keep their instruments warm enough to operate effectively. Since solar power is not available in the darkness of deep space, these craft generate heat from the radioactive decay of small pellets of plutonium dioxide, pictured in the margin. Each pellet is about the size of a pencil eraser and weighs about 2.7 g. If the pellets are pure PuO_2, with the plutonium being ^{238}Pu, what is the activity of one of the fuel pellets, in becquerels?



U.S. Department of Energy/ Photo Researchers

■ **Analysis:** We are looking for the activity of a fuel pellet, and to do this, we will need to know how much material there is and the rate of decay. We can find the number of ^{238}Pu atoms in the sample and then we will need to find the rate constant, k, from the half-life of ^{238}Pu, since it is a first-order process.

■ **Assembling the Tools:** The tool for finding the activity is Equation 21.4. But to use the equation, we'll need the decay constant, k, and the number of plutonium-238 atoms, N, in the fuel pellet.

From Table 21.2, the half-life of ^{238}Pu is 87.8 years. We can rearrange Equation 14.7 to compute the decay constant k from the half-life:

$$k = \frac{\ln 2}{t_{1/2}}$$

We'll want to convert the decay constant into seconds, because the becquerel is defined as disintegrations per second.

We know that the pellet contains 2.7 g of PuO_2. To calculate N, we'll have to perform the following stoichiometric conversion:

$$2.7 \text{ g } PuO_2 \Leftrightarrow \text{? atoms Pu}$$

---

[1] The minus sign is introduced to make the activity a positive number, since the change in the number of radioactive nuclei, ΔN, is negative.

The tools here come from Chapter 4. We'll use the molar mass of PuO_2 (270 g mol^{-1}) to find moles of PuO_2, the chemical formula to relate this to moles of Pu, and then Avogadro's number to find the number of atoms of Pu. Our strategy is to perform the following conversions:

$$2.7\ \text{g PuO}_2 \longrightarrow \text{mol PuO}_2 \longrightarrow \text{mol Pu} \longrightarrow \text{atoms Pu}$$

■ **Solution:** First, let's compute the decay constant from the half-life. We must convert the half-life into seconds:

$$87.8\ \cancel{\text{years}} \times \frac{365\ \cancel{\text{days}}}{1\ \cancel{\text{year}}} \times \frac{24\ \cancel{\text{hours}}}{1\ \cancel{\text{day}}} \times \frac{60\ \cancel{\text{min}}}{1\ \cancel{\text{hour}}} \times \frac{60\ \text{s}}{1\ \cancel{\text{min}}} = 2.77 \times 10^9\ \text{s}$$

Now, we can solve Equation 14.7 for the decay constant:

$$\begin{aligned} k &= \frac{\ln 2}{t_{1/2}} \\ &= \frac{0.693}{2.77 \times 10^9\ \text{s}} \\ &= 2.50 \times 10^{-10}\ \text{s}^{-1} \end{aligned}$$

Next, we need the number of ^{238}Pu atoms in the fuel pellet:

$$2.7\ \cancel{\text{g PuO}_2} \times \frac{1\ \cancel{\text{mol PuO}_2}}{270\ \cancel{\text{g PuO}_2}} \times \frac{1\ \cancel{\text{mol Pu}}}{1\ \cancel{\text{mol PuO}_2}} \times \frac{6.02 \times 10^{23}\ \text{atoms Pu}}{1\ \cancel{\text{mol Pu}}}$$
$$= 6.0 \times 10^{21}\ \text{atoms Pu}$$

From the law of radioactive decay, Equation 21.4, the activity of the fuel pellet is

$$\text{activity} = kN = (2.50 \times 10^{-10}\ \text{s}^{-1}) \times (6.0 \times 10^{21}\ \text{atoms Pu}) = 1.5 \times 10^{12}\ \text{atoms Pu/s}$$

Since the becquerel is defined as the number of disintegrations per second, and each plutonium atom corresponds to one disintegration, we can report the activity as 1.5×10^{12} Bq.

■ **Is the Answer Reasonable?** There is no easy way to check the size of the decay constant beyond checking the arithmetic. The number of Pu atoms in the pellet makes sense, because if we have 2.7 g PuO_2 and the formula mass is 270 g mol^{-1}, we have 1/100th of a mole of PuO_2 and so 1/100 a mole of Pu. We should have (1/100) of 6.02×10^{23} atoms, or 6.02×10^{21} atoms of Pu.

The fuel pellet has about 40 times the activity of a gram of radium-226, as indicated by Equation 21.3, so the activity of ^{238}Pu per gram is about 15 times the activity of ^{226}Ra per gram.

Practice Exercises

21.12 | A 2.00 g sample of a mixture of plutonium with a nonradioactive metal has an activity of 6.22×10^{11} Bq. What is the percentage by mass of plutonium in the sample? (*Hint*: How many atoms of Pu are in the sample?)

21.13 | The EPA limit for radon-222 is 4 pCi (picocuries) per liter of air. How many atoms of ^{222}Rn per liter of air will produce this activity?

■ The *gray* is named after Harold Gray, a British radiologist. *Rad* stands for **r**adiation **a**bsorbed **d**ose.

Nuclear radiation can have varying effects depending on the energy of the radiation and its ability to be absorbed. The **gray (Gy)** is the SI unit of *absorbed dose*, and 1 gray corresponds to 1 joule of energy absorbed per kilogram of absorbing material. The **rad** is an older unit of absorbed dose, where 1 rad is the absorption of 10^{-2} joule per kilogram of tissue. Thus, 1 Gy equals 100 rad. In terms of danger, if every individual in a large population received 4.5 Gy (450 rad), roughly half of the population would die in 60 days.

The gray is not a good basis for comparing the biological effects of radiation in tissue, because these effects depend not just on the energy absorbed but also on the kind of radiation and the tissue itself. The **sievert (Sv)**, the SI unit of *dose equivalent,* was invented to meet this problem. The **rem** is an older unit of dose equivalent, one still used in medicine. Its value is generally taken to equal 10^{-2} Sv. The U.S. government has set guidelines of 0.3 rem per week as the maximum exposure workers may receive. (For comparison, a chest X ray typically involves about 0.004 rem or 4 mrem.) Table 21.3 lists some sources of radiation and their doses.

■ *Rem* stands for **r**oentgen **e**quivalent for **m**an, where the *roentgen* is a unit related to X ray and gamma radiation.

Radiation and Living Tissue

A whole-body dose of 25 rem (0.25 Sv) induces noticeable changes in human blood. A set of symptoms called *radiation sickness* develops at about 100 rem, becoming severe at 200 rem. Among the symptoms are nausea, vomiting, a drop in the white cell count, diarrhea, dehydration, prostration, hemorrhaging, and loss of hair. If each person in a large population absorbed 400 rem, half would die in 60 days. A 600 rem dose would kill everyone in the group in a week. Many workers received at least 400 rem in the moments following the steam explosion that tore apart one of the nuclear reactors at the Ukraine energy park near Chernobyl in 1986.

Table 21.3 Sources of Radiation

Radiation Source	Dose
Living near a nuclear power station	<0.001 rem
Chest X ray	0.004 rem
Cosmic radiation at sea level	0.024 rem
Terrestrial radioactivity	0.028 rem
Mammogram	0.030 rem
Natural radioactivity in the body	0.040 rem
Cosmic radiation living in Denver	0.050 rem
Diagnostic radiology	0.050 rem
Radon in average home	0.200 rem
Gastrointestinal series	1.400 rem

Data from: U.S. EPA Office of Air and Radiation, EPA-402-K-07-006, May 2007.

Free Radical Formation

Even small absorbed doses can be biologically harmful. The danger does not lie in the heat energy associated with the dose, which is usually very small. Rather, the harm is in the ability of ionizing radiation to create unstable ions or neutral species with odd (unpaired) electrons, species that can set off other reactions. Water, for example, can interact as follows with ionizing radiation:

$$\text{H}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}—\text{H} \xrightarrow{\text{radiation}} \left[\text{H}—\overset{\cdot}{\underset{\cdot\cdot}{\text{O}}}—\text{H}\right]^{+} + {}^{0}_{-1}e$$

The new cation, $\left[\text{H}—\overset{\cdot}{\underset{\cdot\cdot}{\text{O}}}—\text{H}\right]^{+}$, is unstable and one breakup path is

$$\left[\text{H}—\overset{\cdot}{\underset{\cdot\cdot}{\text{O}}}—\text{H}\right]^{+} \longrightarrow \underset{\text{proton}}{\text{H}^{+}} + \underset{\substack{\text{hydroxyl}\\ \text{radical}}}{:\overset{\cdot}{\underset{\cdot\cdot}{\text{O}}}—\text{H}}$$

The proton might pick up a stray electron to become a hydrogen atom, H•.

Both the hydrogen atom and the hydroxyl radical are examples of **free radicals** (often simply called *radicals*), which are neutral or charged particles having one or more unpaired electrons. They are chemically very reactive. What they do once formed depends on the other chemical species nearby, but radicals can set off a series of totally undesirable chemical reactions inside a living cell. This is what makes the injury from absorbed radiation of far greater magnitude than what the energy alone could inflict. A dose of 600 rem is a lethal dose in a human, but the same dose absorbed by pure water causes the ionization of only one water molecule in every 36 million.

Background Radiation

The presence of radionuclides in nature makes it impossible for us to be free from all exposure to ionizing radiation. Cosmic rays composed of high-energy photons shower on us from the sun and interstellar space. They interact with the air's nitrogen molecules to produce carbon-14, a beta emitter, which enters the food chain via photosynthesis, which converts CO_2 to sugars and starch. From the earth's crust comes the radiation of radionuclides naturally present. The top 40 cm of earth's soil holds an average of 1 gram of radium, an alpha emitter, per square kilometer. Naturally occurring potassium-40, a beta emitter, adds its radiation wherever potassium ions are found in the body. The presence of carbon-14 and potassium-40 together produce about 5×10^5 nuclear disintegrations per minute inside an adult human. Radon gas seeps into basements from underground formations. In fact, the World Nuclear Organization estimates that a little over half of the radiation we experience, on average, is from radon-222 and its decay products.

Diagnostic X rays, both medical and dental, also expose us to ionizing radiation. All of these sources produce a combined **background radiation** that averages 360 mrem per person annually in the United States. The averages are roughly 82% from natural radiation and 18% from medical sources.

Radiation Protection

Gamma radiation and X rays are so powerful that they are effectively shielded only by very dense materials, like lead. Otherwise, one should stay as far from a source as possible, because the intensity of radiation diminishes with the *square* of the distance. This relationship is the **inverse square law**, which can be written mathematically as follows, where *d* is the distance from the source:

$$\text{Radiation intensity} \propto \frac{1}{d^2}$$

■ When the ratio is taken, the proportionality constant cancels, so we don't have to know what its value is.

When the intensity, I_1, is known at distance d_1, then the intensity I_2 at distance d_2 can be calculated by Equation 21.5:

TOOLS

Inverse square law

$$\frac{I_1}{I_2} = \frac{d_2^2}{d_1^2} \qquad (21.5)$$

This law applies only to a small source that radiates equally in all directions, with no intervening shields.

Practice Exercises

21.14 | If the intensity of radiation from a radioactive sources is 4.8 units at a distance of 5.0 m, how far from the source would you have to move to reduce the intensity to 0.30 unit? (*Hint*: How does intensity vary with distance?)

21.15 | If an operator 10 m from a small source is exposed to 1.4 units of radiation, what will be the intensity of the radiation if he moves to 1.2 m from the source?

21.7 | Medical and Analytical Applications of Radionuclides

Because chemical properties depend on the number and arrangement of orbital electrons and not on the specific makeup of nuclei, both radioactive and stable isotopes of an element behave the same chemically. This fact forms the basis for some uses of radionuclides. The chemical and physical properties enable scientists to get radionuclides into place in systems of interest. Then the radiation is exploited for medical or analytical purposes. Tracer analysis, neutron activation analysis, and radiological dating are three examples we will discuss.

Tracer Analysis

In **tracer analysis,** the chemical form and properties of a radionuclide enable the system to distribute it to a particular location. The intensity of the radiation then tells something about how that site is working. In the form of the iodide ion, for example, iodine-131 is carried by the body to the thyroid gland, the only user of iodide ion in the body. The thyroid takes up the iodide ion to synthesize the hormone thyroxine. The activity of the thyroid can be monitored since an underactive thyroid gland is unable to concentrate iodide ion normally and will emit less intense radiation than a normal thyroid.

Tracer analyses are also used to pinpoint the locations of brain tumors, which are uniquely able to concentrate the pertechnetate ion, TcO_4^-, made from technetium-99*m*.[2] This strong gamma emitter, which resembles the chloride ion in some respects, is one of the most widely used radionuclides in medicine.

■ Technetium-99*m* is also used in bone scans to detect and locate bone cancer. Active cancer sites concentrate the Tc, which can be detected using external scanning devices.

Neutron Activation Analysis

A number of stable nuclei can be changed into emitters of gamma radiation by capturing neutrons, and this makes possible a procedure called **neutron activation analysis**. Neutron capture followed by gamma emission can be represented by the following equation, where *A* is a mass number and *X* is a hypothetical atomic symbol:

$$\underset{\substack{\text{isotope of}\\ \text{element}\\ X\text{ being}\\ \text{analyzed}}}{{}^{A}X} + \underset{\text{neutron}}{{}^{1}_{0}n} + \longrightarrow \underset{\substack{\text{compound}\\ \text{nucleus}\\ \text{(unstable)}}}{{}^{(A+1)}X^{*}} \longrightarrow \underset{\substack{\text{more stable}\\ \text{form of a new}\\ \text{isotope of } X}}{{}^{(A+1)}X} + \underset{\substack{\text{gamma}\\ \text{radiation}}}{{}^{0}_{0}\gamma}$$

A neutron-enriched compound nucleus emits gamma radiation at its own set of unique frequencies, and these sets of frequencies are now known for each isotope. (Not all isotopes, however, become gamma emitters by neutron capture.) The element can be identified by measuring the specific *frequencies* of gamma radiation emitted. The *concentration* of the element can be determined by measuring the *intensity* of the gamma radiation.

Neutron activation analysis is so sensitive that concentrations as low as $10^{-9}\%$ can be determined. A museum might have a lock of hair of some famous but long-dead person suspected of having been slowly murdered by arsenic poisoning. If so, some arsenic would be in the hair, and neutron activation analysis could find it without destroying the specimen of hair.

Radiological Dating

The determination of the age of a geological deposit or an archaeological find by the use of the radionuclides that are naturally present is called **radiological dating**. It is based partly on the premise that the half-lives of radionuclides have been constant throughout the entire geological period. This premise is supported by the finding that half-lives are insensitive to all environmental forces such as heat, pressure, magnetism, or electrical stresses. Radiological dating of archaeological objects by carbon-14 analyses was described in Chapter 14 (page 659).

In geological dating, a pair of isotopes is sought that are related as a "parent" to a "daughter" in a radioactive disintegration series, like the uranium-238 series (Figure 21.7). Uranium-238 (as "parent") and lead-206 (as "daughter") have thus been used as a radiological dating pair of isotopes. The half-life of uranium-238 is very long, a necessary criterion for geological dating. Put simply, after the concentrations of uranium-238 and lead-206 are determined in a rock specimen, the *ratio* of the concentrations together with the half-life of uranium-238 is used to calculate the age of the rock. This works since there is no lead in magma, and rocks come from magma.

Probably the most widely used isotopes for dating rock are the potassium-40/argon-40 pair. Potassium-40 is a naturally occurring radionuclide with a half-life nearly as long as that of uranium-238. One of its modes of decay is electron capture in which argon-40 is formed:

$${}^{40}_{19}\text{K} + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}\text{Ar}$$

---

[2] The *m* in technetium-99*m* means that the isotope is in a metastable form. Its nucleus is at a higher energy level than the nucleus in technetium-99, to which technetium-99*m* decays.

The argon produced by this reaction remains trapped within the crystal lattices of the rock and is freed only when the rock sample is melted. How much has accumulated is measured with a mass spectrometer (page 66), and the observed ratio of argon-40 to potassium-40, together with the half-life of the parent, permits the age of the specimen to be estimated. Because the half-lives of uranium-238 and potassium-40 are so long, samples have to be at least 300,000 years old for either of the two parent–daughter isotope pairs to provide reliable results.

■ For ^{238}U, $t_{1/2} = 4.51 \times 10^9$ yr
For ^{40}K, $t_{1/2} = 1.3 \times 10^9$ yr

Carbon-14 and the Asian Brown Cloud

As discussed in detail in Chapter 14, measurements of the ^{14}C to ^{12}C ratio in an ancient organic sample, such as an object made of wood or bone, permits calculation of the sample's age.

There are two approaches to carbon-14 dating. The older method, introduced by its discoverer, Willard F. Libby (Nobel Prize in Chemistry, 1960), measures the *radioactivity* of a sample taken from the specimen. The radioactivity is proportional to the concentration of carbon-14.

■ For carbon dating to be accurate, extraordinary precautions must be taken to ensure that specimens are not contaminated by more recent sources of carbon or carbon compounds.

The newer and current method of carbon-14 dating relies on a mass spectrometer that is able to separate the atoms of carbon-14 from the other isotopes of carbon (as well as from nitrogen-14) *and count all of them*, not just the carbon-14 atoms that decay. This approach permits the use of smaller samples (0.5–5 mg vs. 1–20 g for the Libby method), it works at much higher efficiencies, and it gives more precise dates. Objects of up to 70,000 years old can be dated, but the highest accuracy involves systems no older than 7000 years.

Using ^{14}C measurements, scientists determined the origin of the carbon-containing aerosols in the Asian brown cloud. If the particles came from the burning of coal and oil, then the amount of ^{14}C in the sample would be very small since coal and oil are more than 70,000 years old. On the other hand, if the amount of ^{14}C in the samples were measurable, then the age of the carbon could be determined. In this case, the carbon was "young" carbon, so the source of the carbon-containing aerosols had to be recently harvested biomass, or plants.

21.8 | Nuclear Fission and Fusion

Nuclear fission is a process whereby a heavy atomic nucleus splits into two lighter fragments. **Nuclear fusion**, on the other hand, is a process whereby very light nuclei join to form a heavier nucleus. Both processes release large amounts of energy, as we will discuss shortly.

Nuclear Fission Reactions

Because of their electrical neutrality, neutrons penetrate an atom's electron cloud relatively easily and so are able to enter the nucleus. Enrico Fermi discovered in the early 1930s that even slow-moving, *thermal neutrons* can be captured. (Thermal neutrons are those whose average kinetic energy is the same as any other group of particles at room temperature.) When he directed them at a uranium target, he discovered that several different species of nuclei, all much lighter than uranium, were produced.

Without realizing it, what Fermi had observed was the nuclear fission of one particular isotope, uranium-235, present in small concentrations in naturally occurring uranium. The general reaction can be represented as follows.

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow X + Y + b\,{}^{1}_{0}n$$

X and Y can be a large variety of nuclei with intermediate atomic numbers. Over 30 have been identified. The coefficient b has an average value of 2.47, the average number of neutrons produced by fission events. A typical specific fission is

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{236}_{92}\text{U}^{*} \longrightarrow {}^{94}_{36}\text{Kr} + {}^{139}_{56}\text{Ba} + 3\,{}^{1}_{0}n$$

What actually undergoes fission is the compound nucleus of uranium-236. It has 144 neutrons and 92 protons, giving it a neutron-to-proton ratio of roughly 1.6. Initially, the emerging krypton and barium isotopes have the same ratio, and this is much too high for them. The neutron-to-proton ratio for stable isotopes with 36 to 56 protons is nearer 1.2 to 1.3 (Figure 21.8). Therefore, the initially formed, neutron-rich krypton and barium nuclides promptly eject neutrons, called *secondary neutrons,* that generally have much higher energies than thermal neutrons.

An isotope that can undergo fission after neutron capture is called a **fissile isotope**. The naturally occurring fissile isotope of uranium used in reactors is uranium-235, whose abundance among the uranium isotopes today is only 0.72%. Two other fissile isotopes, uranium-233 and plutonium-239, can be made in nuclear reactors.

Nuclear Chain Reactions

The secondary neutrons released by fission become thermal neutrons as they are slowed by collisions with surrounding materials. They can now be captured by unchanged uranium-235 atoms. Because each fission event produces, on the average, more than two new neutrons, the potential exists for a **nuclear chain reaction** (Figure 21.14). A *chain reaction* is a self-sustaining process whereby products from one event cause one or more repetitions of the process.

If the sample of uranium-235 is small enough, the loss of neutrons to the surroundings is sufficiently rapid to prevent a chain reaction. However, at a certain **critical mass** of uranium-235 (i.e., about 50 kilograms), this loss of neutrons is insufficient to prevent a sustained reaction. A virtually instantaneous fission of the sample ensues—in other words, an atomic bomb explosion. To trigger an atomic bomb, therefore, two subcritical masses of uranium-235 (or plutonium-239) are forced together to form a critical mass.

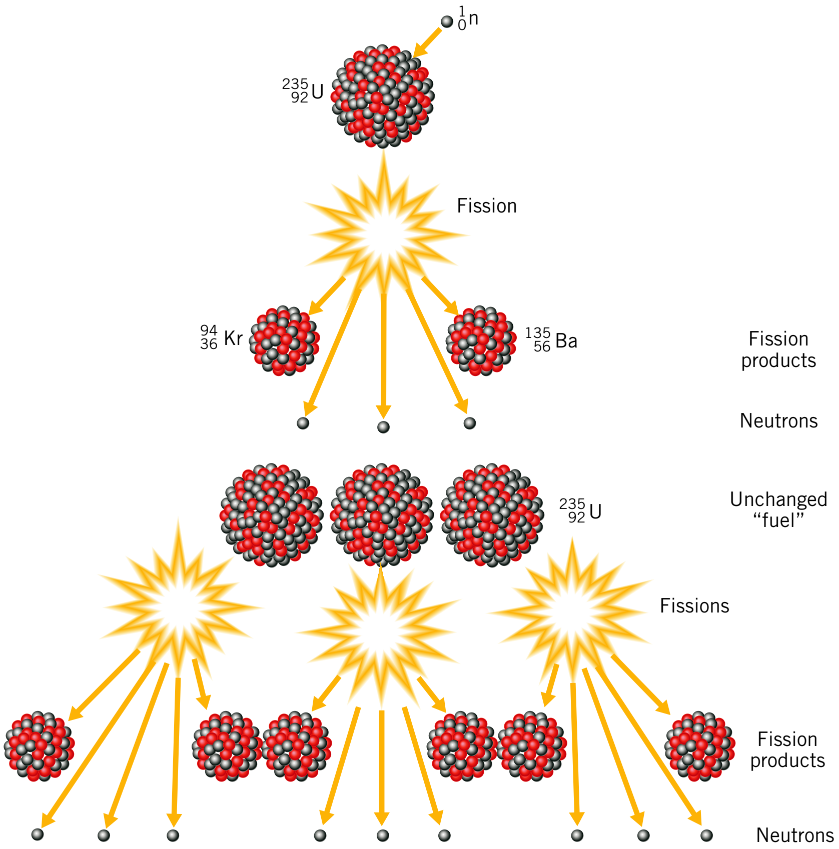


Figure 21.14 | **Nuclear chain reaction.** Whenever the concentration of a fissile isotope is high enough (i.e., at or above the critical mass), the neutrons released by one fission can be captured by enough unchanged nuclei to cause more than one additional fission event. In civilian nuclear reactors, the fissile isotope is too dilute for this to get out of control. In addition, control rods of nonfissile materials that are able to capture excess neutrons can be inserted or withdrawn from the reactor core to make sure that the heat generated can be removed as fast as it forms.

Nuclear Power

The binding energy per nucleon (Figure 21.1) in uranium-235 (about 7.6 MeV) is less than the binding energies of the new nuclides (about 8.5 MeV). The net change for a single fission event can be calculated as follows (where we intend only *two* significant figures in each result):

■ 1 MeV = 1.602×10^{-13} J

Binding energy in krypton-94:

$$(8.5 \text{ MeV/nucleon}) \times 94 \text{ nucleons} = 800 \text{ MeV}$$

Binding energy in barium-139:

$$(8.5 \text{ MeV/nucleon}) \times 139 \text{ nucleons} = \underline{1200 \text{ MeV}}$$

$$\text{Total binding energy of products:} \quad 2000 \text{ MeV}$$

Binding energy in uranium-235:

$$(7.6 \text{ MeV/nucleon}) \times 235 \text{ nucleons} = 1800 \text{ MeV}$$

The difference in total binding energy is (2000 MeV − 1800 MeV), or 200 MeV (3.2×10^{-11} J), which has to be taken as just a rough calculation. This is the energy released by each fission event going by the equation given. The energy produced by the fission of 1 kg (4.25 mole) of uranium-235 is calculated to be roughly 8×10^{13} J, enough to keep a 100 watt light bulb in energy for 3000 years.

■ The energy available from 1 kg of uranium-235 is equivalent to the energy of combustion of 3000 tons of soft coal or 13,200 barrels of oil.

Nuclear Power Plants

Virtually all civilian nuclear power plants throughout the world operate on the same general principles. The energy of fission is used, as heat, either directly or indirectly to increase the pressure of some gas that then drives an electrical generator.

The heart of a nuclear power plant is the *reactor,* where fission takes place in the *fuel core*. The nuclear fuel is generally uranium oxide, enriched to 2–4% in uranium-235 and formed into glasslike pellets. These are housed in long, sealed metal tubes called *cladding*. Groups of tubes are assembled with spacers that permit a coolant to circulate around the tubes. A reactor has several such assemblies in its fuel core. The coolant carries away the heat of fission.

There is no danger of a nuclear power plant undergoing an atomic bomb explosion. An atomic bomb requires uranium-235 at a concentration of 85% or greater or plutonium-239 at a concentration of at least 93%. The concentration of fissile isotopes in a reactor is in the range of 2 to 4%, and much of the remainder is the common, nonfissile uranium-238. However, if the coolant fails to carry away the heat of fission, the reactor core can melt, and the molten mass might even go through the thick-walled containment vessel in which the reactor is kept. Alternatively, the high heat of the fission might split molecules of coolant water into hydrogen and oxygen, which, on recombining, would produce an immense explosion.

To convert secondary neutrons to thermal neutrons, the fuel core has a *moderator*, which is the coolant water itself in nearly all civilian reactors. Collisions between secondary neutrons and moderator molecules heats up the moderator. This heat energy eventually generates steam that enables an electric turbine to run. Ordinary water is a good moderator, but so are heavy water (D_2O) and graphite.

■ D_2O is deuterium oxide. Deuterium is an isotope of hydrogen, ^2_1H.

Two main types of reactors dominate civilian nuclear power: the *boiling water reactor* and the *pressurized water reactor*. Both use ordinary water as the moderator and so are sometimes called *light water reactors*. Roughly two-thirds of the reactors in the United States are the pressurized-water type (Figure 21.15). Such a reactor has two loops, and water circulates in both. The primary loop moves water through the reactor core, where it picks up thermal energy from fission. The water is kept in the *liquid* state by being under high pressure (hence the name *pressurized*-water reactor).

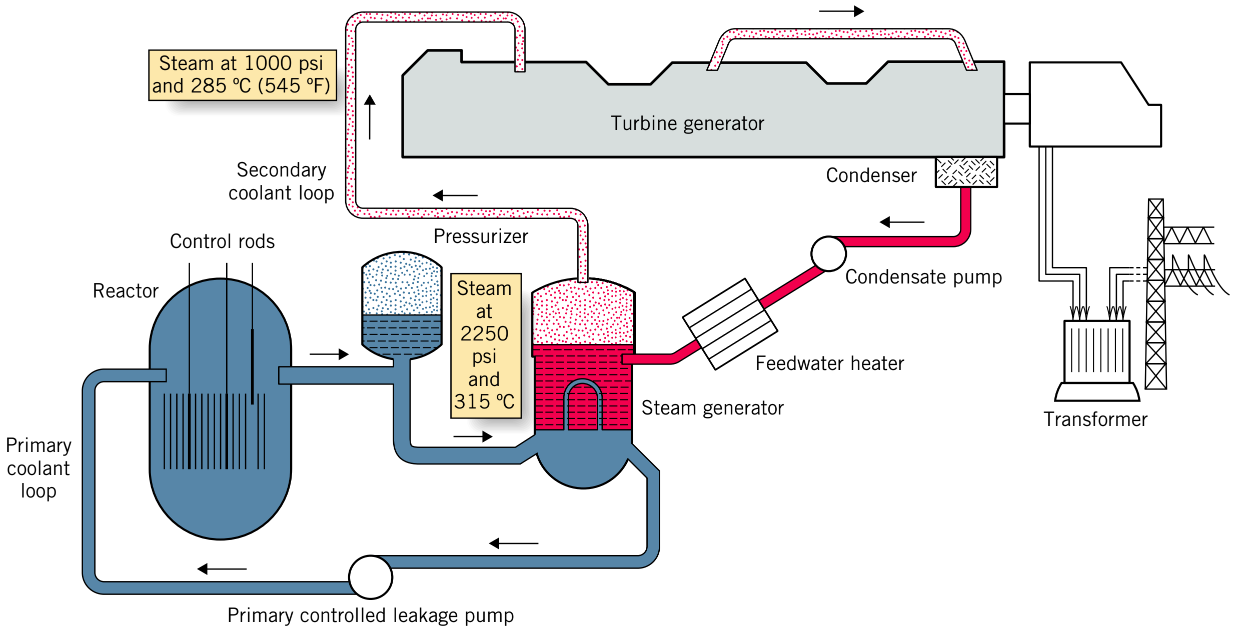


Figure 21.15 | **Pressurized water reactor, the type used in most of the nuclear power plants in the United States.** Water in the primary coolant loop is pumped around and through the fuel elements in the core, and it carries away the heat of the nuclear chain reactions. The hot water delivers its heat to the cooler water in the secondary coolant loop, where steam is generated to drive the turbines. *(Drawing from WASH-1261, U. S. Atomic Energy Commission, 1973.)*

The hot water in the primary loop transfers thermal energy to the secondary loop at the steam generator (Figure 21.15). This makes steam at high temperature and pressure, which is piped to the turbine. As the steam drives the turbine, the steam pressure drops. The condenser at the end of the turbine, cooled by water circulating from a river or lake or from huge cooling towers, forces a maximum pressure drop within the turbine by condensing the steam to liquid water. The returned water is then recycled to high-pressure steam. (In the boiling water reactor, there is only one coolant loop. The water heated in the reactor itself is changed to the steam that drives the turbine.)

Radioactive Waste

Radioactive wastes from nuclear power plants occur as gases, liquids, and solids. The gases are mostly radionuclides of krypton and xenon, but with the exception of xenon-85 ($t_{1/2} = 10.4$ years), the gases have short half-lives and decay quickly. During decay, they must be contained, and this is one function of the cladding. Other dangerous radionuclides produced by fission include iodine-131, strontium-90, and cesium-137.

Iodine-131 must be contained because the human thyroid gland concentrates iodide ion to make the hormone thyroxine. Once the isotope is in the gland, beta radiation from iodine-131 could cause harm, possibly thyroid cancer and possibly impaired thyroid function. An effective countermeasure to iodine-131 poisoning is to take doses of ordinary iodine (as sodium iodide). Statistically, this increases the likelihood that the thyroid will take up stable iodide ion rather than the unstable anion of iodine-131.

■ Cesium-137 has a half-life of 30 years; that of strontium-90 is 28.1 years. Both are beta emitters.

Cesium-137 and strontium-90 also pose problems to humans. Cesium is in Group 1A together with sodium, so radiating cesium-137 cations travel to some of the same places in the body where sodium ions go. Strontium is in Group 2A with calcium, so strontium-90 cations can replace calcium ions in bone tissue, sending radiation into bone marrow and possibly causing leukemia. The half-lives of cesium-137 and strontium-90, however, are relatively short.

Some radionuclides in wastes are so long-lived that solid reactor wastes must be kept away from all human contact for dozens of centuries, longer than any nation has ever yet endured. Probably the most intensively studied procedure for making solid radioactive wastes secure is to convert them to glasslike or rocklike solids, and bury them deeply within a rock stratum or in a mountain believed to be stable on the geological time scale with respect to earthquakes or volcanoes. Finding a location for such a site has been the subject of much scientific and political debate.

Nuclear Fusion

In Section 21.2 we mentioned that joining, or *fusing*, two light nuclei that lie to the left of the peak in the nuclear binding energy curve in Figure 21.1 leads to a net increase in nuclear binding energy and a corresponding release of energy. The process is called *nuclear fusion,* and the amount of energy released is considerably greater than in fission. Harnessing this energy for peaceful purposes is still a long way off, however, because many immensely difficult scientific and engineering problems still remain to be solved.

Deuterium, $^{2}_{1}\text{H}$, an isotope of hydrogen, is a key fuel in all approaches to fusion. It is naturally present as 0.015% of all hydrogen atoms, including those in water. Despite this low percentage, the earth has so much water that the supply of deuterium is virtually limitless.

The fusion reaction most likely to be used in a successful fusion reactor involves the fusion of deuterium and tritium, $^{3}_{1}\text{H}$, another isotope of hydrogen:

$$\underset{\text{deuterium}}{^{2}_{1}\text{H}} + \underset{\text{tritium}}{^{3}_{1}\text{H}} \longrightarrow \underset{\text{helium}}{^{4}_{2}\text{He}} + \underset{\text{neutron}}{^{1}_{0}\text{n}} + 17.6\ \text{MeV}$$

This corresponds to an energy yield of 2.82×10^{-12} J for each atom of helium formed, or 1.70×10^{9} kJ per mole of He formed. One problem with this reaction is that tritium is radioactive with a relatively short half-life, so it doesn't occur naturally. It can be made in several ways, however, from lithium or even deuterium via other nuclear reactions.

Comparing fission and fusion on a mass basis, the fission of one kilogram of ^{235}U yields approximately 8×10^{13} J, whereas forming one kilogram of ^{4}He by the preceding fusion reaction yields 4.2×10^{14} J. Therefore, on a mass basis, fusion yields more than five times as much energy as fission. The potential energy yield from fusion is so great that the deuterium in just 0.005 cubic kilometers of ocean would supply the energy needs of the United States for one year.

Thermonuclear Fusion

The central scientific problem with fusion is to get the fusing nuclei close enough for a long enough time that the nuclear strong force (of attraction) can overcome the electrostatic force (of repulsion). As we learned in Section 21.3, the strong force acts over a much shorter range than the electrostatic force. Two nuclei on a collision course, therefore, repel each other virtually until they touch and get into the range of the strong force. The kinetic energies of two approaching nuclei must therefore be very substantial if they are to overcome this electrostatic barrier. Achieving such energies, moreover, must be accomplished by large numbers of nuclei all at once in batch after batch if there is to be any practical generation of electrical power by nuclear fusion. Relatively isolated fusion events achieved in huge accelerators will not do. The only practical way to give batch quantities of nuclei enough energy is to transfer *thermal* energy to them, and so the overall process is called *thermonuclear fusion.* Temperatures required to provide such thermal energy are very high—namely, more than 100 million degrees Celsius!

The atoms whose nuclei we want to fuse must first be stripped of their electrons. Thus, a high energy cost is exacted from the start but, overall, the energy yield will more than pay for it. The product is an electrically neutral, gaseous mixture of nuclei and unattached electrons called a **plasma**. The plasma must then be made so dense that like-charged nuclei are within 2 fm (2×10^{-15} m) of each other, meaning a plasma density of roughly 200 g cm^{-3} as compared with 200 mg cm^{-3} under ordinary conditions. To achieve this, the plasma must be confined at a pressure of several billion atmospheres long enough for the separate nuclei to fuse. The temperature needed is several times the temperature at the center of our sun.

■ The interior of the sun is at a temperature of approximately 15 million kelvins (15 MK).

Although practical peaceful uses for thermonuclear fusion are still in the distant future, military applications have been around for over 50 years. Thermonuclear fusion is the source of the energy released in the explosion of a hydrogen bomb. The energy needed to trigger the fusion is provided by the explosion of a fission bomb based on either uranium or plutonium.

Fusion in the Sun and Stars

Nature has used thermonuclear fusion since the origin of the universe as the source of energy in stars, where high temperatures (about 15 megakelvins) and huge gravity provide the kinetic energy and high density needed to initiate fusion reactions. The chief process in solar-mass stars is called the proton–proton cycle.

The Proton–Proton Cycle

$$
\begin{array}{ll}
 & 2({}^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H}) \longrightarrow 2\ {}^{2}_{1}\mathrm{H} + 2\ {}^{0}_{1}e + 2\ \nu \\
 & 2({}^{1}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H}) \longrightarrow 2\ {}^{3}_{2}\mathrm{He} + 2\gamma \\
 & {}^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \\
\hline
\text{Net:} & 4\ {}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\ {}^{0}_{1}e + 2\ \nu + 2\gamma
\end{array}
$$

The positrons produced combine with electrons in the plasma, annihilate each other, and generate additional energy and gamma radiation. Virtually all the neutrinos escape the sun and move into the solar system (and beyond), carrying with them a little less than 2% of the energy generated by the cycle. Not counting the energy of the neutrinos, each operation of one cycle generates 26.2 MeV or 4.20×10^{-12} J, which is equivalent to 2.53×10^{12} J per *mole* of alpha particles produced. This is the source of the solar energy radiated throughout our system, which can continue in this way for another 5 billion years.

■ Even at a temperature of 15 megakelvins, the rate of energy production per cubic centimeter by fusion in the sun is only about 10^{-4} J s^{-1} cm^{-3}. (That's thousands of times less than the rate at which a human body generates heat!) But because the sun has such a large volume, the *total* rate of energy production is enormous.

Analyzing and Solving Multi-Concept Problems

Another element formed in the sun is beryllium-7. It has a mass of 7.016928 u. Combustion of how much oil, in kg, would release the same amount of energy as the amount of energy released by the formation of 1.00 kg of ^{7}Be? Since oil is made up of many different compounds, assume that this oil is $C_{20}H_{42}$, which has a ΔH_f° of −2330 kJ/mol.

■ **Analysis** We are being asked to compare two reactions and the energy that they produce. The first reaction is a nuclear reaction, and the amount of energy released in this reaction will need to be used to calculate the amount of material in the second, combustion reaction. The solution will be divided into four parts: (1) for the first reaction, we will determine the binding energy for ^{7}Be, and (2) then we will determine the amount of energy released in that process for 1.00 kg of ^{7}Be. We will then turn our attention to the oil and do the following: (3) find the heat of combustion for $C_{20}H_{42}$ and then (4) the amount of $C_{20}H_{42}$ that gives off the same amount of heat as the ^{7}Be. Alternatively, we could have first calculated the heat of combustion of $C_{20}H_{42}$ and then done the calculations with the ^{7}Be, and finally compared the two to determine the amount of $C_{20}H_{42}$ required.

PART 1

■ **Assembling the Tools** We will find the nuclear binding energy of ^{7}Be from the mass defect using the rest mass of the proton, neutron, and ^{7}Be nucleus.

■ **Solution** We start with the makeup of ^{7}Be and the masses of protons and neutrons. There are four protons and three neutrons in ^{7}Be, and the mass of a proton is 1.007276467 u and the mass of a neutron is 1.0086649156 u.

$$\begin{aligned}\text{For 4 protons: } 4 \times 1.007276467\ \text{u} &= 4.029105868\ \text{u}\\ \text{For 3 neutrons: } 3 \times 1.008664916\ \text{u} &= \underline{3.025994748\ \text{u}}\\ \text{Total rest mass of nucleons in } {}^{7}\text{Be} &= 7.055100616\ \text{u}\end{aligned}$$

The mass defect is calculated from the difference between the mass of the nucleons and the mass of the ^{7}Be nucleus:

$$\underbrace{7.055100616\ \text{u}}_{\text{mass of the 7 nucleons}} - \underbrace{7.016928\ \text{u}}_{\text{mass of nuclei}} = \underbrace{0.038173\ \text{u}}_{\text{mass defect}}$$

PART 2

Assembling the Tools Now that we have the mass defect, we can apply the Einstein equation to calculate the amount of energy equivalent to the mass lost,

$$E = mc^2$$

in which the m is the mass lost, 0.038173 u, and c is the speed of light, $2.9979 \times 10^8\ \text{m s}^{-1}$. After we calculate the energy lost for one atom, we can then calculate it for 1.00 kg of ^{7}Be by converting from one atom to one mole to mass using Avogadro's number and the molar mass of ^{7}Be, respectively.

Solution For Part 2, the first step is using the Einstein equation to calculate the amount of energy released upon the formation of one ^{7}Be nucleus:

$$\begin{aligned}E &= mc^2\\ E &= (0.038173\ \cancel{\text{u}}) \times \frac{1.660654 \times 10^{-27}\ \text{kg}}{1\ \cancel{\text{u}}} \times (2.9979 \times 10^8\ \text{m s}^{-1})^2\\ &= 5.6973 \times 10^{-12}\ \text{kg m}^2\ \text{s}^{-2}\\ &= 5.6973 \times 10^{-12}\ \text{J}\end{aligned}$$

Now we need to calculate the amount of energy released for 1.00 kg of ^{7} Be:

$$\begin{aligned}E &= 1.00\ \cancel{\text{kg }^7\text{Be}} \times \frac{1000\ \cancel{\text{g }^7\text{Be}}}{1\ \cancel{\text{kg }^7\text{Be}}} \times \frac{1\ \cancel{\text{mol }^7\text{Be}}}{7.016928\ \cancel{\text{g }^7\text{Be}}} \times \frac{6.022 \times 10^{23}\ \cancel{\text{atoms }^7\text{Be}}}{1\ \cancel{\text{mol }^7\text{Be}}} \times \frac{5.6973 \times 10^{-12}\ \text{J}}{1\ \cancel{\text{atom }^7\text{Be}}}\\ &= 4.89 \times 10^{14}\ \text{J}\\ &= 4.89 \times 10^{11}\ \text{kJ}\end{aligned}$$

This is the amount of energy released by the formation of 1.00 kg of ^{7} Be.

PART 3

Assembling the Tools Now, we need to find out how much oil will release this much energy upon combustion. We need to start by determining the balanced chemical equation for this process,

$$2\text{C}_{20}\text{H}_{42}(l) + 61\text{O}_2(g) \longrightarrow 40\text{CO}_2(g) + 42\text{H}_2\text{O}(g)$$

Then we must calculate the heat released for this reaction using Hess's law:

$$\Delta H^\circ_{\text{reaction}} = \begin{bmatrix}\text{sum of } \Delta H^\circ_\text{f} \text{ of all}\\ \text{of the products}\end{bmatrix} - \begin{bmatrix}\text{sum of } \Delta H^\circ_\text{f} \text{ of all}\\ \text{of the reactants}\end{bmatrix}$$

Solution We have the balanced chemical equation and the equation for Hess's law, so we can set up the equation:

$$\begin{aligned}\Delta H^\circ = {}&[40\ \text{mol CO}_2(g) \times \Delta H^\circ_{\text{f CO}_2(g)} + 42\ \text{mol H}_2\text{O}(l) \times \Delta H^\circ_{\text{f H}_2\text{O}(l)}]\\ &- [2\ \text{mol C}_{20}\text{H}_{42}(l) \times \Delta H^\circ_{\text{f C}_{20}\text{H}_{42}(l)}]\end{aligned}$$

From Table C.1 in Appendix C, we can find the enthalpies of formation for $CO_2(g)$ and $H_2O(g)$, and use it in the equation:

$$\Delta H^\circ = \left[(40\ \cancel{\text{mol CO}_2(g)}) \times \left(\frac{-393.5\ \text{kJ}}{\cancel{\text{mol CO}_2(g)}}\right) + 42\ \cancel{\text{mol H}_2\text{O}} \times \left(\frac{-241.8\ \text{kJ}}{\cancel{\text{mol H}_2\text{O}}}\right)\right]$$
$$- \left[2\ \cancel{\text{mol C}_{20}\text{H}_{42}} \times \left(\frac{-2330\ \text{kJ}}{\cancel{\text{mol C}_{20}\text{H}_{42}}}\right)\right]$$
$$\Delta H^\circ = -21{,}240\ \text{kJ}$$

This is the amount of heat given off by the combustion of two moles of $C_{20}H_{42}$.

PART 4

Assembling the Tools For the last step in this problem, we have to find out how many kilograms of $C_{20}H_{42}$ will give off 4.89×10^{11} kJ of energy. We have 21,240 kJ of energy given off by the combustion of 2 mol of $C_{20}H_{42}$, so we will have to find the number of moles of $C_{20}H_{42}$ that will give off 4.89×10^{11} kJ, and convert the moles to kilograms.

Solution For this step, we can find the number of moles of $C_{20}H_{42}$ that will give off 4.89×10^{11} kJ:

$$\text{mol C}_{20}\text{H}_{42} = 4.89 \times 10^{11}\ \cancel{\text{kJ}} \times \frac{2\ \text{mol C}_{20}\text{H}_{42}}{2.124 \times 10^4\ \cancel{\text{kJ}}}$$
$$= 4.61 \times 10^7\ \text{mol}$$

Now we can calculate the mass of 4.61×10^7 mol $C_{20}H_{42}$ using the molar mass of $C_{20}H_{42}$:

$$\text{kg C}_{20}\text{H}_{42} = 4.61 \times 10^7\ \cancel{\text{mol C}_{20}\text{H}_{42}} \times \frac{282.6\ \cancel{\text{g C}_{20}\text{H}_{42}}}{1\ \cancel{\text{mol C}_{20}\text{H}_{42}}} \times \frac{1\ \text{kg C}_{20}\text{H}_{42}}{1000\ \cancel{\text{g C}_{20}\text{H}_{42}}}$$
$$= 1.30 \times 10^7\ \text{kg C}_{20}\text{H}_{42}$$

Are the Answers Reasonable? This is an incredibly large number. In order to check that our answer is correct, we should go through the reasoning again.

Summary

The Einstein Equation. Mass and energy are interconvertible, and the **Einstein equation**, $\Delta E = \Delta mc^2$ (where c is the speed of light), lets us calculate one from the other. The total of the energy in the universe and all of the mass calculated as an equivalent of energy is a constant, which is a statement of the **law of conservation of mass–energy**.

Nuclear Binding Energies. When a nucleus forms from its nucleons, some mass changes into energy. This amount of energy, the **nuclear binding energy**, would be required to break up the nucleus again. The higher the binding energy per nucleon, the more stable is the nucleus.

Radioactivity. The *electrostatic force* by which protons repel each other is overcome in the nucleus by the *nuclear strong force*. The ratio of neutrons to protons is a factor in nuclear stability. By radioactivity, the naturally occurring **radionuclides** adjust their neutron/proton ratios, lower their energies, and so become more stable by emitting **alpha** or **beta radiation**, and sometimes gamma radiation as well.

The loss of an **alpha particle** leaves a nucleus with four fewer units of mass number and two fewer of atomic number. Loss of a **beta particle** leaves a nucleus with the same mass number and an atomic number one unit higher. **Gamma radiation** lets a nucleus lose some energy without a change in mass or atomic number. Depending on the specific isotope, synthetic radionuclides emit alpha, beta, and gamma radiation. Some emit **positrons** (positive electrons, a form of **antimatter**) that produce gamma radiation by annihilation collisions with electrons. Other synthetic radionuclides decay by **electron capture** and emit X rays. Some radionuclides emit neutrons.

Nuclear equations are balanced when the mass numbers and atomic numbers on either side of the reaction arrow respectively balance. The energies of emission are usually described in **electron volts (eV)** or multiples thereof, where 1 eV $= 1.602 \times 10^{-19}$ J.

A few very long-lived radionuclides in nature, like ^{238}U, are at the heads of **radioactive disintegration series**, which represent the successive decays of "daughter" radionuclides until a stable isotope forms.

Nuclear Stability. Stable nuclides generally fall within a curving band, called the **band of stability**, when all known nuclides are plotted according to their numbers of neutrons and protons. Radionuclides with neutron/proton ratios that are too high eject beta particles to adjust their ratios downward. Those with neutron/proton ratios that are too low generally emit positrons to change their ratios upward.

Isotopes whose nuclei consist of even numbers of both neutrons and protons are generally much more stable than those with odd numbers of both; this is the **odd–even rule**. Having all neutrons paired and all protons paired is energetically better (i.e., more stable) than having any nucleon unpaired. Isotopes with specific numbers of protons or neutrons, the **magic numbers** of 2, 8, 20, 28, 50, 82, and 126, are generally more stable than others.

Transmutation. When a bombardment particle—a proton, deuteron, alpha particle, or neutron—is captured, the resulting **compound nucleus** contains the energy of both the captured particle and its nucleons. The mode of decay of the compound nucleus is a function of its extra energy, not its extra mass. Many radionuclides have been made by these nuclear reactions, including all of the elements from 93 and higher.

Detecting and Measuring Radiation. Instruments to detect and measure **ionizing radiation—Geiger counters** or **scintillation counters**, for example—take advantage of the ability of radiation to generate ions in air or other matter. Such radiation can harm living tissue by producing **free radicals**.

The **curie (Ci)** and the **becquerel (Bq)**, the SI unit, describe how active a source is; 1 Ci $= 3.7 \times 10^{10}$ Bq where 1 Bq = 1 disintegration/s.

The SI unit of absorbed dose, the **gray (Gy)**, is used to describe how much energy is absorbed by a unit mass of absorber; 1 Gy = 1 J/kg. An older unit, the **rad**, is equal to 0.01 Gy.

The **sievert**, an SI unit, and the **rem**, an older unit, are used to compare doses absorbed by different tissues and caused by different kinds of radiation. A 600 rem whole-body dose is lethal.

The normal **background radiation** causes millirem exposures per year. Naturally occurring radon, cosmic rays, radionuclides in soil and stone building materials, medical X rays, and releases from nuclear tests or from nuclear power plants all contribute to this background.

Protection against radiation can be achieved by using dense shields (e.g., lead or thick concrete), by avoiding the overuse of radionuclides or X rays in medicine, and by taking advantage of the **inverse square law**. This law tells us that the intensity of radiation decreases with the square of the distance from its source.

Applications. **Tracer analysis** uses small amounts of a radionuclide, which can be detected using devices like the scintillation counter, to follow the path of chemical and biological processes. In **neutron activation analysis**, neutron bombardment causes some elements to become γ emitters. The radiation can be detected and measured, giving the identity and concentration of the activated elements. **Radiological dating** uses the known half-lives of naturally occurring radionuclides to date geological and archeological objects.

Fission and Fusion. Uranium-235, which occurs naturally, and plutonium-239, which can be made from uranium-238, are **fissile isotopes** that serve as the fuel in present-day reactors. When either isotope captures a thermal neutron, the isotope splits in one of several ways to give two smaller isotopes plus energy and more neutrons. The neutrons can generate additional fission events, enabling a nuclear chain reaction. If a critical mass of a fissile isotope is allowed to form, the **nuclear chain reaction** proceeds out of control, and the material detonates as an atomic bomb explosion. *Pressurized water reactors* are the most commonly used fission reactors for power generation, and have two loops of circulating fluids. In the primary loop, coolant circulates around the reactor core and absorbs the heat of fission. In the secondary loop, water accepts the heat and changes to high-pressure steam, which drives an electrical generator. One major problem with nuclear energy is the storage of radioactive wastes.

Thermonuclear fusion joins two light nuclei to form a heavier nucleus with the release of more energy than nuclear fission. A typical reaction combines $^{2}_{1}$H and $^{3}_{1}$H to give $^{4}_{2}$He and a neutron. High temperatures and pressures are necessary to initiate the fusion reaction. In stars, gravity is able to contain the high temperature **plasma** and allow fusion to occur. In a hydrogen bomb, the reaction is initiated by a fission bomb. Scientific and engineering hurdles must still be overcome before fusion can be a viable peaceful energy source.

TOOLS

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

The Einstein equation (page 978)

This equation, $\Delta E = \Delta m_0 c^2$ (or often just $E = mc^2$), is used when you have to relate an amount of mass to its equivalent in energy. Be careful of units in using the equation. To obtain joules, mass must be in units of kilograms and c must have units of m/s (because $1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$).

Balancing nuclear equations (page 982)

When you have to write and balance a nuclear equation, remember to apply the following two criteria:

1. The sums of the mass numbers on each side of the arrow must be equal.
2. The sums of the atomic numbers on each side must be the same.

The odd-even rule (page 990)

This rule allows you to judge and compare the likely stability of nuclei according to their numbers of protons and neutrons.

When the numbers of neutrons and protons in a nucleus are both even, the isotope is far more likely to be stable than when both numbers are odd.

Law of radioactive decay (page 995)

Use this law to relate the *activity* (in units of disintegrations per second, or Bq) to the *decay constant, k,* (a first-order rate constant) and the number of atoms of the radionuclide in the sample, N. The activity is a quantity that can be measured using a Geiger or scintillation counter:

$$\text{Activity} = -\frac{\Delta N}{\Delta t} = kN$$

Half-life of a radionuclide (page 995)

When you know the half-life of an isotope (which is available in tables), you can calculate the decay constant, k. This is useful when you need to apply the law of radioactive decay (see above).

$$t_{1/2} = \frac{\ln\ 2}{k}$$

Inverse square law (page 998)

This simple law lets you compute radiation intensity at various distances from a radioactive source. If the intensity, I_1, is known at distance d_1, then the intensity I_2 at distance d_2 can be calculated by

$$\frac{I_1}{I_2} = \frac{d_2^2}{d_1^2}$$

= *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** ILW = An Interactive Learningware solution is available for this problem. OH = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Conservation of Mass and Energy

21.1 In calculations involving chemical reactions, we can regard the law of conservation of mass as a law independent of the law of conservation of energy despite Einstein's union of the two. What fact(s) make(s) this possible?

21.2 How can we know that the speed of light is the absolute upper limit on the speed of any object?

21.3 State the following:

(a) law of conservation of mass–energy

(b) Einstein equation

21.4 What is the difference between the rest mass of a particle and the mass of a particle in motion? Why do we use the rest mass of the particle for most calculations?

Nuclear Binding Energy

21.5 Why isn't the sum of the masses of all nucleons in one nucleus equal to the mass of the actual nucleus?

21.6 Which element has the largest binding energy per nucleon? What happens to the nuclei when the binding energy is too small?

Radioactivity

21.7 When a substance is described as *radioactive*, what does that mean? Why is the term *radioactive decay* used to describe the phenomenon?

21.8 Three kinds of radiation make up nearly all of the radiation observed from naturally occurring radionuclides. What are they?

21.9 Give the composition of each of the following:

(a) alpha particle

(b) beta particle

(c) positron

(d) deuteron

21.10 Why is the penetrating ability of alpha radiation less than that of beta or gamma radiation?

21.11 With respect to their formation, how do gamma rays and X rays differ?

21.12 How does electron capture generate X rays?

21.13 For the process of beta emission, where does the electron originate? What particle emits the electron and what else is formed?

Band of Stability

21.14 What data are plotted and what criterion is used to identify the actual band in the band of stability?

21.15 Both barium-123 and barium-140 are radioactive, but which is more likely to have the *longer* half-life? Explain your answer.

21.16 Tin-112 is a stable nuclide but indium-112 is radioactive and has a very short half-life ($t_{1/2} = 14$ min). What does tin-112 have that indium-112 does not to account for this difference in stability?

21.17 Lanthanum-139 is a stable nuclide but lanthanum-140 is unstable ($t_{1/2} = 40$ hr). What rule of thumb concerning nuclear stability is involved?

21.18 As the atomic number increases, the neutron/proton ratio increases. What does this suggest is a factor in nuclear stability?

21.19 Radionuclides of high atomic number are far more likely to be alpha emitters than those of low atomic number. Offer an explanation for this phenomenon.

21.20 Although lead-164 has two magic numbers, 82 protons and 82 neutrons, this isotope is unknown. Lead-208, however, is known and stable. What problem accounts for the nonexistence of lead-164?

21.21 What decay particle is emitted from a nucleus of low to intermediate atomic number but a relatively high neutron/proton ratio? How does the emission of this particle benefit the nucleus?

21.22 What decay particle is emitted from a nucleus of low to intermediate atomic number but a relatively low neutron/proton ratio? How does the emission of this particle benefit the nucleus?

21.23 Does electron capture increase, decrease, or maintain the neutron/proton ratio in a nucleus? Are radionuclides above or below the band of stability more likely to undergo this change?

Transmutations

21.24 Compound nuclei form and then decay almost at once. What accounts for the instability of a compound nucleus?

21.25 What explains the existence of several decay modes for the compound nucleus aluminum-27?

21.26 Rutherford theorized that a compound nucleus forms when helium nuclei hit nitrogen-14 nuclei. If this compound nucleus decayed by the loss of a neutron instead of a proton, what would be the other product?

21.27 Why is it easier to use neutrons to form compound nuclei rather than alpha particles or other nuclei?

Measuring Radiations

21.28 What specific property of nuclear radiation is used by the Geiger counter?

21.29 Dangerous doses of radiation can actually involve very small quantities of energy. Explain.

21.30 What units, SI and common, are used to describe each of the following?

(a) the *activity* of a radioactive sample

(b) the *energy* of a particle or of a photon of radiation given off by a nucleus

(c) the amount of energy absorbed by a given mass by a dose of radiation

(d) dose equivalents for comparing biological effects

21.31 Explain the necessity in health sciences for the *sievert*.

21.32 Which is more dangerous: ingesting a radioactive compound with a short half-life or a radioactive compound with a long half-life if the compound can be eliminated from the body within a day?

Applications of Radionuclides

21.33 Why should a radionuclide used in diagnostic work have a short half-life? If the half-life is too short, what problem arises?

21.34 An alpha emitter is not used in diagnostic work. Why?

21.35 In general terms, explain how neutron activation analysis is used and how it works.

21.36 What is one assumption in the use of the uranium/lead ratio for dating ancient geologic formations?

***21.37** If a sample used for carbon-14 dating is contaminated by air, there is a potentially serious problem with the method. What is it?

21.38 List some of the kinds of radiation that make up our background radiation.

Nuclear Fission and Fusion

21.39 What do each of the following terms mean?

(a) thermal neutron

(b) nuclear fission

(c) fissile isotope

(d) nuclear fusion

21.40 Which fissile isotope occurs in nature?

21.41 What fact about the fission of uranium-235 makes it possible for a *chain reaction* to occur?

21.42 Explain in general terms why fission generates more neutrons than needed to initiate it.

21.43 Why would there be a *subcritical mass* of a fissile isotope? (Why isn't *any* mass of uranium-235 critical?)

21.44 What purpose is served by a *moderator* in a nuclear reactor?

21.45 Why is there no possibility of an atomic bomb explosion from a nuclear power plant?

21.46 Write the nuclear equation for the fusion reaction between deuterium and tritium. Why must tritium be synthesized for this reaction?

21.47 What obstacles make constructing a reactor for controlled nuclear fusion especially difficult?

Review Problems

Conservation of Mass and Energy

***21.48** Calculate the mass in kilograms of a 1.00 kg object when its velocity, relative to us, is **(a)** 3.00×10^7 m s^{-1}, **(b)** 2.90×10^8 m s^{-1}, and **(c)** 2.99×10^8 m s^{-1}. (Notice the progression of these numbers toward the velocity of light, 3.00×10^8 m s^{-1}.)

***21.49** Calculate the velocity, relative to us, in m s^{-1} of an object with a rest mass, m_0, of 1.000 kg when its mass, m, is **(a)** 1.005 kg, **(b)** 1.1 kg, and **(c)** 5.0 kg.

21.50 Calculate the mass equivalent in grams of 1.00 kJ of energy.

21.51 Calculate the energy equivalent in kJ of 1.00 g of mass.

OH **21.52** Calculate the amount of mass in nanograms that is changed into energy when one mole of liquid water forms by the combustion of hydrogen, all measurements being made at 1 atm and 25 °C. What percentage is this of the total mass of the reactants?

21.53 Show that the mass equivalent of the energy released by the complete combustion of 1 mol of methane (890 kJ) is 9.89 ng.

Nuclear Binding Energies

ILW OH **21.54** Calculate the binding energy in J/nucleon of the deuterium nucleus whose mass is 2.0135 u.

21.55 Calculate the binding energy in J/nucleon of the tritium nucleus whose mass is 3.01550 u.

21.56 What is the mass defect for copper-63 if the mass of the nucleus is 62.9529601 u? Calculate the binding energy for Cu-63.

21.57 What is the mass defect for americium-241 if the mass of the nucleus is 241.05682 u? Calculate the binding energy for Am-241.

Radioactivity

21.58 Complete the following nuclear equations by writing the symbols of the missing particles:

(a) ${}^{211}_{82}\text{Pb} \longrightarrow {}^{0}_{-1}e + \_\_\_\_\_$

(b) ${}^{177}_{73}\text{Ta} \xrightarrow{\text{Electron capture}} \_\_\_\_\_$

(c) ${}^{220}_{86}\text{Rn} \longrightarrow {}^{4}_{2}\text{He} + \_\_\_\_\_$

(d) ${}^{19}_{10}\text{Ne} \longrightarrow {}^{0}_{1}e + \_\_\_\_\_$

21.59 Write the symbols of the missing particles to complete the following nuclear equations:

(a) ${}^{245}_{96}\text{Cm} \longrightarrow {}^{4}_{2}\text{He} + \_\_\_\_\_$

(b) ${}^{146}_{56}\text{Ba} \longrightarrow {}^{0}_{-1}e + \_\_\_\_\_$

(c) ${}^{58}_{29}\text{Cu} \longrightarrow {}^{0}_{1}e + \_\_\_\_\_$

(d) ${}^{68}_{32}\text{Ge} \xrightarrow{\text{Electron capture}} \_\_\_\_\_$

OH **21.60** Write a balanced nuclear equation for each of the following changes:

(a) alpha emission from plutonium-242

(b) beta emission from magnesium-28

(c) positron emission from silicon-26

(d) electron capture by argon-37

OH **21.61** Write the balanced nuclear equation for each of the following nuclear reactions:

(a) electron capture by iron-55

(b) beta emission by potassium-42

(c) positron emission by ruthenium-93

(d) alpha emission by californium-251

21.62 Write the symbols, including the atomic and mass numbers, for the radionuclides that would give each of the following products:

(a) fermium-257 by alpha emission

(b) bismuth-211 by beta emission

(c) neodymium-141 by positron emission

(d) tantalum-179 by electron capture

21.63 Each of the following nuclides forms by the decay mode described. Write the symbols of the parents, giving both atomic and mass numbers:

(a) rubidium-80 formed by electron capture

(b) antimony-121 formed by beta emission

(c) chromium-50 formed by positron emission

(d) californium-253 formed by alpha emission

21.64 Krypton-87 decays to krypton-86. What other particle forms?

21.65 Write the symbol of the nuclide that forms from cobalt-58 when it decays by electron capture.

Band of Stability

OH **21.66** If an atom of potassium-38 had the option of decaying by positron emission or beta emission, which route would it likely take, and why? Write the balanced nuclear equation.

21.67 Suppose that an atom of argon-37 could decay by either beta emission or electron capture. Which route would it likely take, and why? Write the balanced nuclear equation.

21.68 What is the most probable decay process for polonium-209? Write the balanced nuclear equation.

21.69 What is the most probable decay process for silicon-32? Write the balanced nuclear equation.

21.70 If we begin with 3.00 mg of iodine-131 ($t_{1/2} = 8.07$ hr), how much remains after six half-life periods?

21.71 A sample of technetium-99*m* with a mass of 9.00 ng will have decayed to how much of this radionuclide after four half-life periods (about 1 day)?

Transmutations

21.72 When vanadium-51 captures a deuteron (${}^{2}_{1}\text{H}$), what compound nucleus forms? (Write its symbol.) This particle expels a proton (${}^{1}_{1}p$). Write the balanced nuclear equation for the overall change from vanadium-51.

21.73 The alpha-particle bombardment of fluorine-19 generates sodium-22 and neutrons. Write the balanced nuclear equation, including the intermediate compound nucleus.

OH **21.74** Gamma-ray bombardment of bromine-81 causes a transmutation in which a neutron is one product. Write the symbol of the other product.

21.75 Neutron bombardment of cadmium-115 results in neutron capture and the release of gamma radiation. Write the balanced nuclear equation.

21.76 When manganese-55 is bombarded by protons, each ^{55}Mn nucleus releases a neutron. What else forms? Write the balanced nuclear equation.

21.77 Which nuclide forms when sodium-23 is bombarded by alpha particles and the compound nucleus emits a gamma ray photon?

21.78 The nuclei of which isotope of zinc would be needed as bombardment particles to make nuclei of element 112 from lead-208 if the intermediate compound nucleus loses a neutron?

21.79 Write the symbol of the nuclide whose nuclei would be the target for bombardment by nickel-64 nuclei to produce nuclei of ${}^{272}_{111}\text{Rg}$ after the intermediate compound nucleus loses a neutron.

Measuring Radiations

21.80 Suppose that a radiologist who is 2.0 m from a small, unshielded source of radiation receives 2.8 units of radiation. To reduce the exposure to 0.28 units of radiation, to what distance from the source should the radiologist move?

21.81 By what percentage should a radiation specialist increase the distance from a small unshielded source to reduce the radiation intensity by 10.0%?

OH **21.82** If exposure from a distance of 1.60 m gave a worker a dose of 8.4 rem, how far should the worker move away from the source to reduce the dose to 0.50 rem for the same period?

21.83 During work with a radioactive source, a worker was told that he would receive 55 mrem at a distance of 4.0 m during 30 min of work. What would be the received dose if the worker moved closer, to 0.50 m, for the same period?

21.84 A sample giving 3.7×10^{10} disintegrations per second has what activity in Ci and in Bq?

21.85 A sample of a radioactive metal used in medicine has an activity of 3.5 mCi. What is its activity in Bq and how many disintegrations/s does it give?

21.86 Smoke detectors contain a small amount of americium-241, which has a half-life of 1.70×10^5 days. If the detector contains 0.20 mg of ^{241}Am, what is the activity, in becquerels? In microcuries?

21.87 Strontium-90 is a dangerous radioisotope present in fallout produced by nuclear weapons. ^{90}Sr has a half-life of 1.00×10^4 days. What is the activity of 1.00 g of ^{90}Sr, in becquerels? In microcuries?

21.88 Iodine-131 is a radioisotope present in radioactive fallout that targets the thyroid gland. If 1.00 mg of ^{131}I has an activity of 4.6×10^{12} Bq, what is the decay constant for ^{131}I? What is the half-life, in seconds?

21.89 A 10.0 mg sample of thallium-201 has an activity of 7.9×10^{13} Bq. What is the decay constant for ^{201}Tl? What is the half-life of ^{201}Tl, in seconds?

Applications of Radionuclides

OH **21.90** What percentage of cesium chloride made from cesium-137 (beta emitter, $t_{1/2} = 30.1$ y) remains after 150 y? What *chemical* product forms?

21.91 A sample of waste has a radioactivity, caused solely by strontium-90 (beta emitter, $t_{1/2} = 28.1$ yr), of $0.245\ \mathrm{Ci\ g^{-1}}$. How many years will it take for its activity to decrease to $1.00 \times 10^{-6}\ \mathrm{Ci\ g^{-1}}$?

21.92 A worker in a laboratory unknowingly became exposed to a sample of radio-labeled sodium iodide made from iodine-131 (beta emitter, $t_{1/2} = 8.07$ day). The mistake was realized 28.0 days after the accidental exposure, at which time the activity of the sample was 25.6×10^{-5} Ci/g. The safety officer needed to know how active the sample was at the time of the exposure. Calculate this value in Ci/g.

21.93 Technetium-99*m* (gamma emitter, $t_{1/2} = 6.02$ hr) is widely used for diagnosis in medicine. A sample prepared in the early morning for use that day had an activity of 4.52×10^{-6} Ci. What will its activity be at the end of the day—that is, after 8.00 hr?

21.94 A 0.500 g sample of rock was found to have 2.45×10^{-6} mol of potassium-40 ($t_{1/2} = 1.3 \times 10^9$ yr) and 2.45×10^{-6} mol of argon-40. How old was the rock? (What assumption is made about the origin of the argon-40?)

21.95 If a rock sample was found to contain 1.16×10^{-7} mol of argon-40, how much potassium-40 would also have to be present for the rock to be 1.3×10^9 years old?

21.96 A tree killed by being buried under volcanic ash was found to have a ratio of carbon-14 atoms to carbon-12 atoms of 4.8×10^{-14}. How long ago did the eruption occur?

21.97 A wooden door lintel from an excavated site in Mexico would be expected to have what ratio of carbon-14 to carbon-12 atoms if the lintel is 9.0×10^3 y old?

Nuclear Fission and Fusion

OH **21.98** Complete the following nuclear equation by supplying the symbol for the other product of the fission.

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow {}^{94}_{38}\mathrm{Sr} + \underline{\qquad} + 2\,{}^{1}_{0}n$$

21.99 Both products of the fission in Problem 21.98 are unstable. According to Figures 21.8 and 21.9, what is the most likely way for each of them to decay: by alpha emission, beta emission, or positron emission? Explain. What are some of the possible fates of the extra neutrons produced by the fission shown in Problem 21.98?

Additional Exercises

21.100 The age of “young” groundwater can be determined by measuring the ratio of tritium to helium-3 in water. If “young” groundwater is no more than 40 years old, what percent of tritium will remain in water at 40 years? The amount of ^{3}He in the water is also measured at the same time as the amount of tritium. What would the sum of the moles of tritium and ^{3}He represent?

21.101 What is the balanced nuclear equation for each of the following changes?

(a) beta emission from aluminum-30

(b) alpha emission from einsteinium-252

(c) electron capture by molybdenum-93

(d) positron emission by phosphorus-28

*21.102 Calculate to five significant figures the binding energy in J/nucleon of the nucleus of an atom of iron-56. The observed mass of one *atom* is 55.9349 u. Which figure in this chapter lets us know that no isotope has a *larger* binding energy per nucleon?

21.103 Give the balanced nuclear equation for each of the following changes:

(a) positron emission by carbon-10

(b) alpha emission by curium-243

(c) electron capture by vanadium-49

(d) beta emission by oxygen-20

*21.104 If a positron is to be emitted spontaneously, how much more *mass* (as a minimum) must an *atom* of the parent have than an *atom* of the daughter nuclide? Explain.

*21.105 If a proton and an antiproton were to collide and produce two annihilation photons, what would the wavelength of the photons be, in meters? Which of the decimal multipliers in Table 2.4 (page 35) would be most appropriate for expressing this wavelength?

21.106 There is a gain in binding energy per nucleon when light nuclei fuse to form heavier nuclei. However, a tritium atom and a deuterium atom, in a mixture of these isotopes, does not spontaneously fuse to give helium (and energy). Explain why not.

21.107 ^{214}Bi decays to isotope *A* by alpha emission; *A* then decays to *B* by beta emission, which decays to *C* by another beta emission. Element *C* decays to *D* by still another beta emission, and *D* decays by alpha emission to a stable isotope, *E*. What is the proper symbol of element *E*? (Contributed by Prof. W. J. Wysochansky, Georgia Southern University.)

21.108 ^{15}O decays by positron emission with a half-life of 124 s. **(a)** Give the proper symbol of the product of the decay. **(b)** How much of a 750 mg sample of ^{15}O remains after 5.0 min of decay? (Contributed by Prof. W. J. Wysochansky, Georgia Southern University.)

21.109 Alpha decay of ^{238}U forms ^{234}Th. What kind of decay from ^{234}Th produces ^{234}Ac? (Contributed by Prof. Mark Benvenuto, University of Detroit–Mercy.)

21.110 A sample of rock was found to contain 2.07×10^{-5} mol of ^{40}K and 1.15×10^{-5} mol of ^{40}Ar. If we assume that all of the ^{40}Ar came from the decay of ^{40}K, what is the age of the rock in years? ($t_{1/2} = 1.3 \times 10^9$ years for ^{40}K)

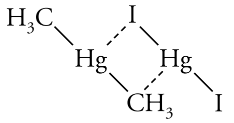
21.111 The ^{14}C content of an ancient piece of wood was found to be one-tenth of that in living trees. How many years old is this piece of wood? ($t_{1/2} = 5730$ years for ^{14}C.)

21.112 Dinitrogen trioxide, N_2O_3, is largely dissociated into NO and NO_2 in the gas phase where there exists the equilibrium,

$$N_2O_3 \rightleftharpoons NO + NO_2$$

In an effort to determine the structure of N_2O_3, a mixture of NO and $^*NO_2$ was prepared containing isotopically labeled N in the NO_2. After a period of time the mixture was analyzed and found to contain substantial amounts of both $^*NO$ and $^*NO_2$. Explain how this is consistent with the structure for N_2O_3 being ONONO.

21.113 The reaction, $(CH_3)_2Hg + HgI_2 \longrightarrow 2CH_3HgI$, is believed to occur through a transition state with the structure,



If this is so, what should be observed if CH_3HgI and $^*HgI_2$ are mixed, where the asterisk denotes a radioactive isotope of Hg? Explain your answer.

*21.114 A large, complex piece of apparatus has built into it a cooling system containing an unknown volume of cooling liquid. The volume of the coolant needs to be measured without draining the lines. To the coolant was added 10.0 mL of methanol whose molecules included atoms of ^{14}C and that had a specific activity (activity per gram) of 580 counts per minute per gram (cpm/g), determined using a Geiger counter. The coolant was permitted to circulate to assure complete mixing before a sample was withdrawn that was found to have a specific activity of 29 cpm/g. Calculate the volume of coolant in the system in milliliters. The density of methanol is 0.792 g/mL, and the density of the coolant is 0.884 g/mL.

21.115 Iodine-131 is used to treat Graves disease, a disease of the thyroid gland. The amount of ^{131}I used depends on the size of the gland. If the dose is 86 microcuries per gram of thyroid gland, how many grams of ^{131}I should be administered to a patient with a thyroid gland weighing 20 g? Assume all the iodine administered accumulates in the thyroid gland.

21.116 The fuel for a thermonuclear bomb (hydrogen bomb) is lithium deuteride, a salt composed of the ions ${}^{6}_{3}Li^+$ and ${}^{2}_{1}H^-$. Considering the nuclear reaction

$${}^{6}_{3}\text{Li} + {}^{1}_{1}n \longrightarrow {}^{4}_{2}\text{He} + {}^{3}_{1}\text{H}$$

explain how a ^{235}U fission bomb could serve as a trigger for a fusion bomb. Write appropriate balanced nuclear equations.

21.117 In 2006, the synthesis of ${}^{294}_{118}Uuo$ (an isotope of element 118) was reported to involve the bombardment of ^{245}Cf with ^{48}Ca. Write an equation for the nuclear reaction, being sure to include any other products of the reaction.

*21.118 Radon, a radioactive noble gas, is an environmental problem in some areas, where it can seep out of the ground and into homes. Exposure to radon-222, an α emitter with a half-life of 3.823 days, can increase the risk of lung cancer. At an exposure level of 4 pCi per liter (the level at which the EPA recommends action), the lifetime risk of death from lung cancer due to radon exposure is estimated to be 62 out of 1000 for current smokers, compared with 73 out of 10,000 for nonsmokers. If the air in a home was analyzed and found to have an activity of 4.1 pCi L^{-1}, how many atoms of ^{222}Rn are there per liter of air?

***21.119** The isotope ^{145}Pr decays by emission of beta particles with an energy of 1.80 MeV each. Suppose a person swallowed, by accident, 1.0 mg of Pr having a specific activity (activity per gram) of 140 Bq/g. What would be the absorbed dose from ^{145}Pr in units of Gy and rad over a period of 10 minutes? Assume all of the beta particles are absorbed by the person's body.

21.120 Why is the isotope ^{36}Cl radioactive while ^{35}Cl and ^{37}Cl are not? The isotope decays by beta emission, what isotope is formed? Write the nuclear equation that shows the process.

Multi-Concept Questions

***21.121** A complex ion of chromium(III) with oxalate ion was prepared from ^{51}Cr-labeled $K_2Cr_2O_7$, having a specific activity of 843 cpm/g (counts per minute per gram), and ^{14}C-labeled oxalic acid, $H_2C_2O_4$, having an specific activity of 345 cpm/g. Chromium-51 decays by electron capture with the emission of gamma radiation, whereas ^{14}C is a pure beta emitter. Because of the characteristics of the beta and gamma detectors, each of these isotopes may be counted independently. A sample of the complex ion was observed to give a gamma count of 165 cpm and a beta count of 83 cpm. From these data, determine the number of oxalate ions bound to each Cr(III) in the complex ion. (*Hint*: For the starting materials calculate the cpm per mole of Cr and oxalate, respectively.)

21.122 Iridium-192, a beta emitter, is used in medicine to treat certain cancers. The ^{192}Ir is used as a wire and inserted near the tumor for a given amount of time and then removed. The ^{192}Ir wire is coated with pure platinum, and is sold by diameter and amount of radiation emitted. One type of wire sold is 140 mm long, has a linear apparent activity of 30–130 MBq/cm, an active diameter (which is the iridium-192) of 0.1 mm, and an outer diameter (the platinum) of 0.3 mm. How much ^{192}Ir is in the wire if the apparent activity is 30 MBq/cm? If the wire is placed in the tumor for 50 hours, how much radiation is absorbed by the tumor? The wire is shipped in lead tubes—why?

Exercises in Critical Thinking

21.123 A silver wire coated with nonradioactive silver chloride is placed into a solution of sodium chloride that is labeled with radioactive ^{36}Cl. After a while, the AgCl was analyzed and found to contain some ^{36}Cl. How do you interpret the results of this experiment?

21.124 Suppose you were given a piece of cotton cloth and told that it was believed to be 2000 years old. You performed a carbon dating test on a tiny piece of the cloth and your data indicated that it was only 800 years old. If the cloth really was 2000 years old, what factors might account for your results?

21.125 In 2006, the former Soviet spy Alexander Litvinenko was poisoned by the polonium isotope ^{210}Po. He died 23 days after ingesting the isotope, which is an alpha emitter. Find data on the Internet to answer the following: Assuming Litvinenko was fed 1 μg of ^{210}Po and that it became uniformly distributed through the cells in his body, how many atoms of ^{210}Po made their way into each cell in his body? (Assume his body contained the average number of cells found in an adult human.) Also, calculate the number of cells affected by the radiation each second, being sure to take into account an estimate of the average number of cells affected by an alpha particle emitted by a ^{210}Po nucleus.

21.126 What would be the formula of the simplest hydrogen compound of element 116? Would a solution of this compound in water be acidic, basic, or neutral? Explain your reasoning.

21.127 Astatine is a halogen. Its most stable isotope, ^{110}At, has a half-life of only 8.3 hours, and only very minute amounts of the element are ever available for study ($<$0.001 μg). This amount is so small as to be virtually invisible. Describe experiments you might perform that would tell you whether the silver salt of astatine, AgAt, is insoluble in water.

22 Metal Complexes

Chapter Outline

22.1 | Complex Ions
22.2 | Metal Complex Nomenclature
22.3 | Coordination Number and Structure
22.4 | Isomers of Metal Complexes
22.5 | Bonding in Metal Complexes
22.6 | Biological Functions of Metal Ions

The horseshoe crab—considered a living fossil—has blue blood, while humans have red blood. The color of the blood is influenced by the metal compounds that are found in blood. The blood of horseshoe crabs contains hemocyanin, a copper-containing protein that transports oxygen, whereas human blood uses hemoglobin, which is iron based, to carry oxygen. In this chapter, we will look at how metals are bonded to other ions and molecules and how the color of the compounds are affected by the metal and its bonds. Rick Poley/Visuals Unlimited

This Chapter in Context

In previous chapters you learned many of the concepts that chemists have used to develop an understanding of how the elements react with each other and the kinds of compounds they produce. For example, in our discussions of chemical kinetics, you learned how various factors affect the rates of reactions, and in our study of thermodynamics you learned how enthalpy and entropy changes affect the possibility of observing chemical changes. Our focus, however, was primarily on the concepts themselves, with examples of chemical behavior being used to reinforce and justify them. With all of these concepts available to us now, we will direct our emphasis in the opposite direction and examine some of the physical and chemical properties of the compounds of metals.

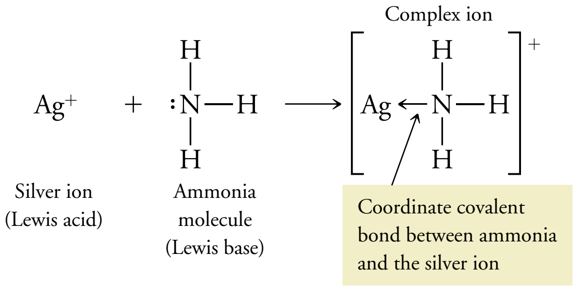
This chapter is devoted to an in-depth look at complex ions of metals, a topic first introduced in Chapter 18. These substances, which have applications from food preservatives to catalyzing biochemical reactions, have a variety of structures and colors. We will study the kinds of substances that combine with metals to form complexes, how complexes are named, and how the electronic structures and colors of complexes can be explained.

22.1 | Complex Ions

In Section 18.4 (page 855), we introduced you to **complex ions** (or more simply, **complexes**) of metals. Recall that these are substances formed when molecules or anions become bonded covalently to metal ions to form more complex species. Two examples that were given were the pale blue $Cu(H_2O)_6^{2+}$ ion and the deep blue $Cu(NH_3)_4^{2+}$ ion. In Chapter 18, we discussed how the formation of complex ions can affect the solubilities of salts, but the importance of these substances reaches far beyond solubility equilibria. The number of complex ions formed by metals, especially the transition metals, is enormous, and the study of the properties, reactions, structures, and bonding in complexes like $Cu(NH_3)_4^{2+}$ has become an important specialty within chemistry. The study of metal complexes even extends into biochemistry—for example, the metal ions in the horseshoe crab pictured in the chapter opener. This is because, ultimately, nearly all of the metals in our bodies become bound in complexes in order to perform their biochemical functions.

Before we proceed further, let's consider some of the basic terminology we will use in our discussions. The molecules or ions that become attached to a metal ion [e.g., the NH_3 molecules in $Cu(NH_3)_4^{2+}$] are called **ligands.** Ligands are either neutral molecules or anions that contain one or more atoms with at least one unshared electron pair that can be donated to the metal ion in the formation of a metal–ligand bond. The reaction of a ligand with a metal ion is therefore a Lewis acid–base reaction in which the ligand is the Lewis base (the electron pair donor) and the metal ion is the Lewis acid (the electron pair acceptor).

■ Recall that a coordinate covalent bond is one in which both of the shared electrons originate on the same atom. Once formed, of course, a coordinate covalent bond is just like any other covalent bond.


Complex ion
Ag+
+
H
:N—H
H
Ag ← N—H
+
Silver ion (Lewis acid)
Ammonia molecule (Lewis base)
Coordinate covalent bond between ammonia and the silver ion

A ligand atom that donates an electron pair to the metal is said to be a **donor atom** and the metal is the **acceptor**. Thus, in the preceding $AgNH_3^+$ example, the nitrogen of the ammonia molecule is the donor atom and the silver ion is the acceptor. Because of the way the metal–ligand bond is formed, it can be considered to be a covalent bond, and compounds that contain metal complexes are often called **coordination compounds**. The complexes themselves are sometimes referred to as **coordination complexes.**

Types of Ligands

Ligands, whether they are anions or neutral molecules, are *Lewis bases.* As a result, they contain at least one atom with one or more lone pairs (unshared pairs) of electrons.

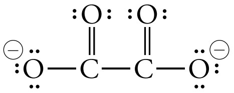
Anions that serve as ligands include many simple monatomic ions, such as the halide ions (F^-, Cl^-, Br^-, and I^-) and the sulfide ion (S^{2-}). Common polyatomic anions that are ligands are nitrite ion (NO_2^-), cyanide ion (CN^-), hydroxide ion (OH^-), thiocyanate ion (SCN^-), and thiosulfate ion ($S_2O_3^{2-}$). (This is really only a small sampling, not a complete list.)

The most common neutral molecule that serves as a ligand is water, and most of the reactions of metal ions in aqueous solutions are actually reactions of their complex ions—ions in which the metal is attached to some number of water molecules. Copper(II) ions,[1] for example, form the complex ion $Cu(H_2O)_6^{2+}$, and cobalt(II) also combines with water molecules to form $Co(H_2O)_6^{2+}$. Another common neutral ligand is ammonia, NH_3, which has one lone pair of electrons on the nitrogen atom. If ammonia is added to an aqueous solution containing the $Ni(H_2O)_6^{2+}$ ion, for example, the color changes dramatically from green to blue as ammonia molecules displace water molecules (see Figure 22.1):

$$\underset{\text{(green)}}{Ni(H_2O)_6^{2+}(aq)} + 5NH_3(aq) \longrightarrow \underset{\text{(blue)}}{Ni(NH_3)_5(H_2O)^{2+}(aq)} + 5H_2O$$

Each of the ligands that we have discussed so far is able to use just one atom to attach itself to a metal ion. Such ligands are called **monodentate ligands**, indicating that they have only "one tooth" with which to "bite" the metal ion.

There are also many ligands that have two or more donor atoms, and collectively they are referred to as **polydentate ligands**. The most common of these have two donor atoms, so they are called **bidentate ligands**. When they form complexes, *both* donor atoms become attached to the same metal ion. Oxalate ion and ethylenediamine (abbreviated *en* in writing the formula for a complex) are examples of bidentate ligands.



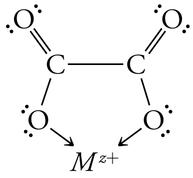
$$\ominus\,:\ddot{\underset{..}{O}}-\overset{\overset{:\ddot{O}:}{\|}}{C}-\overset{\overset{:\ddot{O}:}{\|}}{C}-\ddot{\underset{..}{O}}:\,\ominus$$

oxalate ion

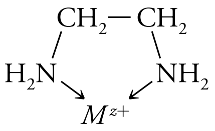
$$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$$

ethylenediamine, en

When these ligands become attached to a metal ion, the following ring structures are formed:



an oxalate complex



an ethylenediamine complex

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[1] The formula $Cu(H_2O)_6^{2+}$ is actually an oversimplification. Copper(II) complexes in water usually have two water molecules loosely attached to the Cu^{2+} at a greater distance than the other four ligand atoms. Therefore, the copper(II) complex with water could also be written $Cu(H_2O)_4^{2+}$ to indicate the water molecules more strongly bound to the Cu^{2+} ion.

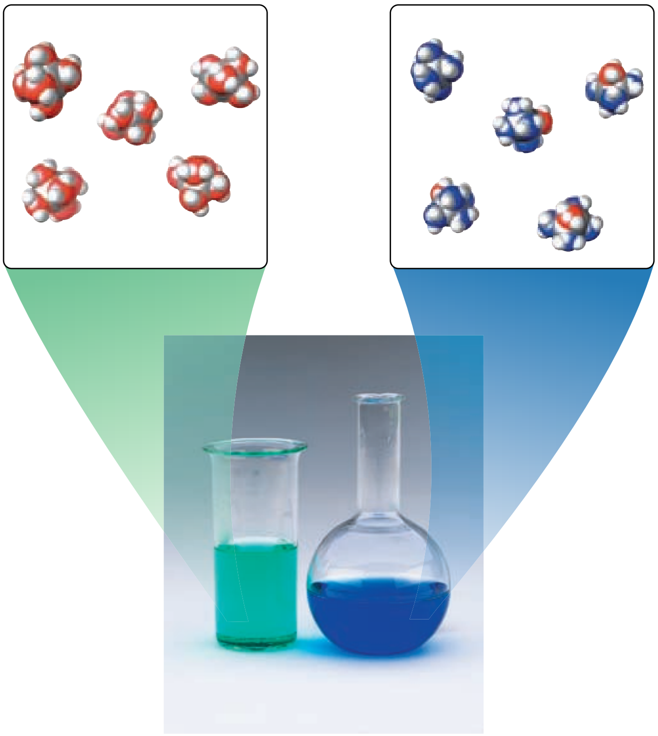
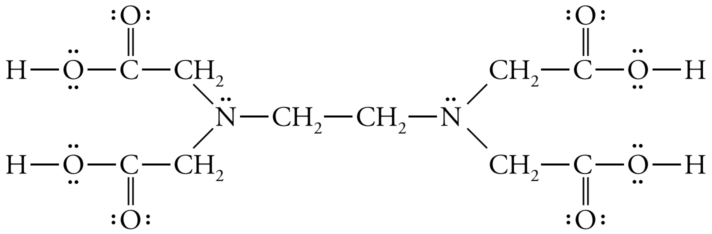


Figure 22.1 | **Complex ions of nickel.** (*Left*) A solution of nickel chloride, which contains the green $Ni(H_2O)_6^{2+}$ ion. (*Right*) Adding ammonia to the nickel chloride solution forms the blue $Ni(NH_3)_5(H_2O)^{2+}$ ion. *(Andy Washnik)*

Complexes that contain such ring structures are called **chelates**.[2] Structures like these are important in "complex ion chemistry," as we shall see later in this chapter.

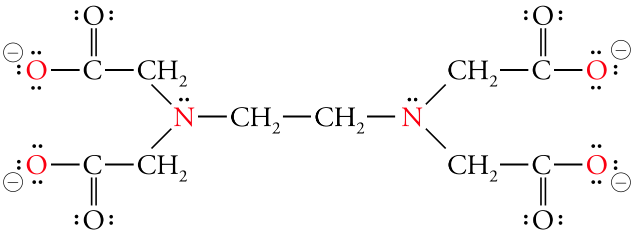
One of the most common polydentate ligands is a compound called ethylenediaminetetraacetate, mercifully abbreviated $EDTA^{4-}$ (or Y^{4-} by analytical chemists).

■ Sometimes the ligand $EDTA^{4-}$ is abbreviated using small letters—that is, $edta^{4-}$.

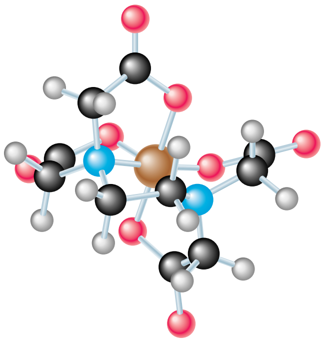


Ethylenediaminetetraacetic acid, H_4EDTA)

The H atoms attached to the oxygen atoms are easily removed as protons, which gives an anion with a charge of 4−. The structure of the anion, $EDTA^{4-}$, is as follows with the donor atoms in red:



$EDTA^{4-}$



The structure of an EDTA complex. The nitrogen atoms are blue, oxygen is red, carbon is black, and hydrogen is white. The metal ion is in the center of the complex bonded to the two nitrogens and four oxygens.

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[2] The term *chelate* comes from the Greek *chele*, meaning claw. These bidentate ligands grasp the metal ions with two "claws" (donor atoms) somewhat like a crab holds its prey. (Who says scientists have no imagination?)

The $EDTA^{4-}$ ion has six donor atoms, and this permits it to wrap itself around a metal ion and form very stable complexes.

EDTA is a particularly useful and important ligand. It is relatively nontoxic, which allows it to be used in small amounts in foods to retard spoilage. If you look at the labels on bottles of salad dressings, for example, you often will find that one of the ingredients is $CaNa_2EDTA$ (calcium disodium EDTA). The $EDTA^{4-}$ available from this salt forms soluble complex ions with any traces of metal ions that might otherwise promote reactions of the salad oils with oxygen, and thereby lead to spoilage.

■ The *calcium* salt of EDTA is used because the $EDTA^{4-}$ ion would otherwise extract Ca^{2+} ions from bones, and that would be harmful.

Many shampoos contain Na_4EDTA to soften water. The $EDTA^{4-}$ binds to Ca^{2+}, Mg^{2+}, and Fe^{3+} ions, which removes them from the water and prevents them from interfering with the action of detergents in the shampoo. A similar application was described in the *Chemistry Outside the Classroom 18.1* on page 858.

EDTA is also sometimes added in small amounts to whole blood to prevent clotting. It ties up calcium ions, which the clotting process requires. EDTA has even been used as a treatment in cases of heavy metal poisoning because it can help remove the poisonous heavy metal ions, like Hg^{2+} and Pb^{2+}, from the body when they have been accidentally ingested.

Writing Formulas for Metal Complexes

When we write the formula for a complex, we utilize the following rules:

TOOLS

Rules for writing formulas for complexes

1. The symbol for the metal ion is always given first, followed by the ligands.
2. When more than one kind of ligand is present, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order).
3. The charge on the complex is the algebraic sum of the charge on the metal ion and the charges on the ligands.
4. The formula is placed inside of square brackets with the charge of the complex as a superscript outside the brackets, if it is not zero.

■ Square brackets here do not mean molar concentration. It is usually clear from the context of a discussion whether we intend the brackets to mean molarity or a chemical formula.

For example, the formula of the complex ion of Cu^{2+} and NH_3, which we mentioned earlier, was written $[Cu(NH_3)_4]^{2+}$ with the Cu first followed by the ligands. The charge on the complex is 2+ because the copper ion has a charge of 2+ and the ammonia molecules are neutral. Copper(II) ion also forms $[Cu(CN)_4]^{2-}$, a complex ion with four cyanide ions, CN^-. The metal ion contributes two (+) charges and the four ligands contribute a total of four (−) charges, one for each cyanide ion. The algebraic sum is therefore −2, so the complex ion has a charge of 2−.

The brackets emphasize that the ligands are attached to the metal ion and are not free to roam about. One of the many complex ions formed by the chromium(III) ion contains five water molecules and one chloride ion as ligands. To indicate that all are attached to the Cr^{3+} ion, we use brackets and write the complex ion as $[CrCl(H_2O)_5]^{2+}$. When this complex is isolated as a chloride salt, the formula is written $[CrCl(H_2O)_5]Cl_2$, in which $[CrCl(H_2O)_5]^{2+}$ is the cation and so is written first. The formula $[CrCl(H_2O)_5]Cl_2$ shows that five water molecules and a chloride ion are bonded to the chromium ion, and the other two chloride ions are said to be **counter ions**, meaning they are present to provide electrical neutrality for the salt.

In Chapter 1, you learned about hydrates, and one was the beautiful blue hydrate of copper(II) sulfate, $CuSO_4 \cdot 5H_2O$. It was much too early then to make the distinction, but the formula should have been written as $[Cu(H_2O)_4]SO_4 \cdot H_2O$ to show that four of the five water molecules are held in the crystal as part of the complex ion $[Cu(H_2O)_4]^{2+}$. The fifth water molecule is held in the crystal by being hydrogen bonded to the sulfate ion.

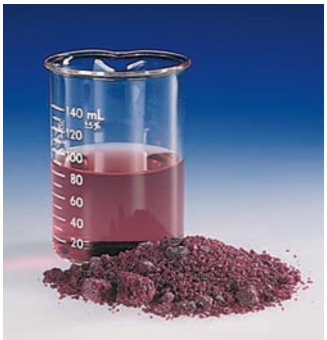

Figure 22.2 | **Color of the cobalt(II) ion in hexahydrate salts.** The ion $[Co(H_2O)_6]^{2+}$ is pink and gives its color both to crystals and to an aqueous solution of $CoCl_2 \cdot 6H_2O$. *(Michael Watson)*

Many other hydrates of metal salts actually contain complex ions of the metals in which water is the ligand. Cobalt salts like cobalt(II) chloride, for example, crystallize from aqueous solutions as hexahydrates (meaning they contain six H_2O molecules per formula unit of the salt). The compound $CoCl_2 \cdot 6H_2O$ (Figure 22.2) actually is $[Co(H_2O)_6]Cl_2$, and it contains the pink complex $[Co(H_2O)_6]^{2+}$. This ion also gives solutions of cobalt(II) salts a pink color as can be seen in Figure 22.2. Although most hydrates of metal salts contain complex ions, the distinction is seldom made, and it's acceptable to write the formula for these hydrates in the usual fashion—for example, $CuSO_4 \cdot 5H_2O$ instead of $[Cu(H_2O)_4]SO_4 \cdot H_2O$.

Example 22.1
Writing the Formula for a Complex Ion

Write the formula for the complex ion formed by the metal ion Cr^{3+} and six NO_2^- ions as ligands. Decide whether the complex could be isolated as a chloride salt or a potassium salt, and write the formula for the appropriate salt.

■ **Analysis:** In this question, we are being asked to determine the formula, including charge, for the complex ion with one Cr^{3+} and six NO_2^-. The net charge on the complex ion will determine whether the salt will be with chloride or potassium. If the complex is a positive ion, it would require a negative ion to form a salt, so it could be isolated as a chloride salt; if the complex is a negative ion, then a potassium salt could form.

■ **Assembling the Tools:** The rules on page 1020 are the tools we'll use to write the formula of the complex ion correctly.

■ **Solution:** Six NO_2^- ions contribute a total charge of 6−; the metal contributes a charge of 3+. The algebraic sum is $(6-) + (3+) = 3-$. The formula of the complex ion is therefore $[Cr(NO_2)_6]^{3-}$.

Because the complex is an anion, it requires a cation to form a neutral salt, so the complex could be isolated as a potassium salt, not as a chloride salt. For the salt to be electrically neutral, three K^+ ions are required for each complex ion, $[Cr(NO_2)_6]^{3-}$. The formula of the salt would therefore be $K_3[Cr(NO_2)_6]$. Notice that in writing the formula for the salt, we've specified the cation (K^+) first, followed by the anion.

■ **Is the Answer Reasonable?** Things to check: Have we written the formula with the metal ion first, followed by the ligands? Have we computed the charge on the complex correctly? Does the formula for the salt correspond to an electrically neutral substance? The answer to each question is yes, so all seems to be okay.

Practice Exercises

22.1 | Write the formula of the complex ion formed by Ag^+ and two thiosulfate ions, $S_2O_3^{2-}$. If we were able to isolate this complex ion as its ammonium salt, what would be the formula for the salt? (*Hint*: Remember, salts are electrically neutral.)

22.2 | Aluminum chloride crystallizes from aqueous solutions as a hexahydrate. Write the formula for the salt and suggest a formula for the complex ion formed by aluminum ion and water.

22.3 | What is the formula of the complex ion that is formed from chromium(III), four water molecules, and two chloride ions? Is the counter ion more likely to be a halide or an alkali metal?

The Chelate Effect

An interesting aspect of the complexes formed by bidentate ligands such as ethylenediamine and oxalate ion is that their stabilities are higher as compared to similar complexes formed by monodentate ligands. For example, the complex $[Ni(en)_3]^{2+}$ is considerably more stable than $[Ni(NH_3)_6]^{2+}$, even though both complexes have six nitrogen atoms bound to a Ni^{2+} ion. We can compare them quantitatively by examining their formation constants:

■ Ammonia, a monodentate ligand, supplies one donor atom to a metal. Ethylenediamine (en), a bidentate ligand, has two nitrogen donor atoms. Therefore, six ammonia molecules and three ethylenediamine molecules supply the same number of donor atoms.

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) \qquad K_{form} = 2.0 \times 10^8$$
$$Ni^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) \qquad K_{form} = 4.1 \times 10^{17}$$

The ethylenediamine complex is more stable than the ammonia complex by a factor of 2×10^9 (2 billion)! This exceptional stability of complexes formed with polydentate ligands is called the **chelate effect**, so named because it occurs in compounds in which the ligands have two or more sites that bind to one metal center. A ring forms involving the metal and the ligand, and extra stability is gained if the ring has five or six atoms in it.

There are two related reasons for the chelate effect, which we can understand best if we examine the ease with which the complexes undergo dissociation once formed. One reason appears to be associated with the probability of the ligand leaving the vicinity of the metal ion when the donor atom becomes detached. If one end of a bidentate ligand comes loose from the metal, the donor atom cannot wander very far because the other end of the ligand is still attached. There is a high probability that the loose end will become reattached to the metal ion before the other end can let go, so overall the ligand appears to be bound tightly. With a monodentate ligand, however, there is nothing to hold the ligand near the metal ion if it becomes detached. The ligand can easily move off into the surrounding solution and be lost. As a result, a monodentate ligand is not as firmly attached to the metal ion as a polydentate ligand.

The second reason is related to the entropy change for the dissociation. In Chapter 19 you learned that when there is an increase in the number of particles in a chemical reaction, the entropy change is positive. Dissociation of both complexes produces more particles, so the entropy change is positive for both of them. However, comparing the two reactions,

$$[\mathrm{Ni(NH_3)_6}]^{2+}(aq) \rightleftharpoons \mathrm{Ni}^{2+}(aq) + 6\mathrm{NH_3}(aq) \qquad K_{\mathrm{inst}} = 5.0 \times 10^{-9}$$

$$[\mathrm{Ni(en)_3}]^{2+}(aq) \rightleftharpoons \mathrm{Ni}^{2+}(aq) + 3\mathrm{en}(aq) \qquad K_{\mathrm{inst}} = 2.4 \times 10^{-18}$$

we see that dissociation of the ammonia complex gives a net increase of *six* in the number of particles, whereas dissociation of the ethylenediamine complex yields a net increase of *three*. This means the entropy change is more positive for the dissociation of the ammonia complex than for the ethylenediamine complex. The larger entropy change translates into a more favorable $\Delta G°$ for the decomposition, so at equilibrium the ammonia complex should be dissociated to a greater extent. This is, in fact, what is suggested by the values of their instability constants, K_{inst} (recall from Section 18.5 that $K_{\mathrm{inst}} = 1/K_{\mathrm{form}}$).

■ Recall that $\Delta G°$ is related to the equilibrium constant. A more favorable $\Delta G°$ for dissociation should yield a larger equilibrium constant, and, indeed, we find the instability constant is larger for the ammonia complex.

Table 22.1 Some Common Ligands

Name as a Ligand	Formula[a]
acetato	CH_3COO^-
ammine	NH_3
aqua	H_2O
azido	N_3^-
bromo	Br^-
cyano	CN^-
chloro	Cl^-
ethylenediamine (en)	$NH_2CH_2CH_2NH_2$
hydroxo	OH^-
iodo	I^-
nitrito	$ON\underline{O}^-$
nitro	$O\underline{N}O^-$
oxalato (ox^{2-})	$COOCOO^{2-}$
sulfido	S^{2-}
thiosulfato	$S_2OO_2^{2-}$

[a] The underlined elements are the ones that bond to the metal ions.

A list of ligands is given in Table 22.1. The atom that binds to the metal is underlined. Some ligands can bind through different atoms; for example, the NO_2^- ion can bind either through the N or through the O.

22.2 | Metal Complex Nomenclature

The naming of chemical compounds was introduced in Chapter 3, where we discussed the nomenclature system for simple inorganic compounds. This system, revised and kept up to date by the International Union of Pure and Applied Chemistry (IUPAC), has been extended to cover metal complexes. Below are some of the rules that have been developed to name coordination complexes. As you will see, some of the names arrived at following the rules are difficult to pronounce at first, and may even sound a little odd. However, the primary purpose of this and any other system of nomenclature is to provide a method that gives each compound its own unique name and permits us to write the formula of the compound given the name.

Rules of Nomenclature for Coordination Complexes

Rules for naming complexes

1. **Cationic species are named before anionic species.** This is the same rule that applies to other ionic compounds such as NaCl, where we name the cation first, followed by the anion (i.e., sodium chloride).
2. **The names of anionic ligands always end in the suffix -o.**
   (a) Ligands whose names end in *-ide* usually have this suffix changed to *-o*.

Anion		Ligand
chloride	Cl^-	chloro-
bromide	Br^-	bromo-
cyanide	CN^-	cyano-
oxide	O^{2-}	oxo-

■ Names such as chloro and bromo in the table at the left are the ones traditionally used and are acceptable. Strict IUPAC names simply drop the -e and replace it with -o to give chlorido, bromido, etc. Thus, S^{2-} would be named sulfido as a ligand.

   (b) Ligands whose names end in *-ite* or *-ate* become *-ito* and *-ato*, respectively.

Anion		Ligand
carbonate	CO_3^{2-}	carbonato-
thiosulfate	$S_2O_3^{2-}$	thiosulfato-
thiocyanate	SCN^-	thiocyanato- (when bonded through sulfur)
		isothiocyanato- (when bonded through nitrogen)
oxalate	$C_2O_4^{2-}$	oxalato-
nitrite	NO_2^-	nitrito- (when bonded through oxygen; written ONO in the formula for the complex)[a]

[a] An exception to this is when the nitrogen of the NO_2^- ion is bonded to the metal, in which case the ligand is named nitro-.

3. **A neutral ligand is given the same name as the neutral molecule.** Thus, the molecule ethylenediamine, when serving as a ligand, is called ethylenediamine in the name of the complex. Two very important exceptions to this, however, are water and ammonia. These are named as follows when they serve as ligands:

   H_2O aqua NH_3 ammine (note the double *m*)

4. **When there is more than one of a particular ligand, their number is specified by the prefixes di- = 2, tri- = 3, tetra- = 4, penta- = 5, hexa- = 6, and so forth. When confusion might result by using these prefixes, the following are used instead: bis = 2, tris = 3, and tetrakis = 4.** Following this rule, the presence of two chloride ligands in a complex would be indicated as *dichloro-* (notice, too, the ending on the ligand name). However, if two ethylenediamine ligands are present, use of the prefix *di-* might cause confusion. Someone reading the name might wonder whether diethylenediamine means two ethylenediamine molecules or one molecule of a substance called diethylenediamine. To avoid this problem we place the ligand name in parentheses preceded by *bis*; that is, *bis(ethylenediamine)*.

■ *Bis-* is employed here so that if the name is used in verbal communication it is clear that the meaning is two ethylenediamine molecules.

5. **In the *formula* of a complex, the symbol for the metal is written first, followed by those of the ligands. Among the ligands, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order). In the *name* of the complex, the ligands are named first, in alphabetical order *without regard to charge*, followed by the name of the metal**. For example, suppose we had a complex composed of Co^{3+}, two Cl^- (chloro- ligands), one CN^- (cyano- ligand), and three NH_3 (ammine- ligands). The formula of this electrically neutral complex would be written $[CoCl_2(CN)(NH_3)_3]$. In the name of this complex, the ligands would be

specified before the metal as *triamminedichlorocyano-* (*triammine-* for the three NH_3 ligands, *dichloro* for the two Cl^- ligands, and *cyano-* for the CN^- ligand). When alphabetizing the names of the ligands, we ignore the prefixes *tri-* and *di-*. Thus, *triammine-* is written before *dichloro-* because *ammine-* precedes *chloro-* alphabetically. For the same reason, *dichloro-* is written before *cyano*. The complete name for the complex is given below under Rule 7.

■ The ligands are alphabetized according to the first letter of the name of the ligand, not the first letter of the numbering prefix.

6. **Negative (anionic) complex ions always end in the suffix *-ate*.** This suffix is appended to the English name of the metal atom in most cases. However, if the name of the metal ends in *-ium, -um,* or *-ese*, the ending is dropped and replaced by *-ate*.

Metal	Metal as Named in an Anionic Complex
aluminum	aluminate
chromium	chromate
manganese	manganate
nickel	nickelate
cobalt	cobaltate
zinc	zincate
platinum	platinate
vanadium	vanadate

For metals whose symbols are derived from their Latin names, the suffix *-ate* is appended to the Latin stem. (An exception, however, is mercury; in an anion it is named *mercurate.*)

Metal	Stem	Metal as Named in an Anionic Complex
iron	ferr-	ferrate
copper	cupr-	cuprate
lead	plumb-	plumbate
silver	argent-	argentate
gold	aur-	aurate
tin	stann-	stannate

For neutral or positively charged complexes, the metal is *always* specified with the English name for the element, *without any suffix*.

7. **The oxidation state of the metal in the complex is written in Roman numerals within parentheses following the name of the metal.**[3] For example,

$[CoCl_2(CN)(NH_3)_3]$ is triamminedichlorocyanocobalt(III)

$[Co(NH_3)_6]^{3+}$ is the hexaamminecobalt(III) ion

$[CuCl_4]^{2-}$ is the tetrachlorocuprate(II) ion

No spaces

Notice that there are no spaces between the names of the ligands and the name of the metal, and that there is no space between the name of the metal and the parentheses that enclose the oxidation state expressed in Roman numerals.

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[3] Alternatively, the charge on the complex as a whole can be used instead of the oxidation number—for example, tetrachloridocuprate(2−).

The following are some additional examples. Study them carefully to see how the nomenclature rules apply. Then try the practice exercises that follow.

$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) ion
$K_3[CoCl_6]$	potassium hexachlorocobaltate(III)
$[CoCl_2(NH_3)_4]^+$	tetraamminedichlorocobalt(III) ion
$Na_3[Co(NO_2)_6]$	sodium hexanitrocobaltate(III)
$[Ag(NH_3)_2]^+$	diamminesilver(I) ion
$[Ag(S_2O_3)_2]^{3-}$	dithiosulfatoargentate(I) ion
$[Mn(en)_3]Cl_2$	tris(ethylenediamine)manganese(II) chloride
$[PtCl_2(NH_3)_2]$	diamminedichloroplatinum(II)

■ Notice, once again, that the alphabetical order of the ligands is determined by the first letter in the name of the ligand, not the first letter in the prefix.

Practice Exercises

22.4 | Write the formula for each of the following: (a) hexachlorostannate(IV) ion, (b) ammonium diaquatetracyanoferrate(II), and (c) dibromobis(ethylenediamine)osmium(II). (*Hint*: Divide each name into its various parts.)

22.5 | Name the following compounds: (a) $K_3[Fe(CN)_6]$, (b) $[CrCl_2(en)_2]_2SO_4$, and (c) $[Co(H_2O)_6]_2[CrF_6]$ (in which the cobalt is in the +2 oxidation state).

22.3 | Coordination Number and Structure

One of the most interesting aspects of the study of complexes is the kinds of structures that they form. In many ways, this is related to the **coordination number** of the metal ion, which we define as *the number of donor atoms attached to the metal ion*. For example, in the complex $[Ni(CN)_4]^{2-}$, four cyanide ions bind the nickel ion, so the coordination number of Ni^{2+} in this complex is 4. Similarly, the coordination number of Cr^{3+} in the $[Cr(H_2O)_6]^{3+}$ ion is 6, and the coordination number of Ag^+ in $[Ag(NH_3)_2]^+$ is 2.

Sometimes the coordination number isn't immediately obvious from the formula of the complex. For example, you learned that there are many polydentate ligands that contain more than one donor atom that can bind simultaneously to a metal ion. Often, a metal is able to accommodate two or more polydentate ligands to give complexes with formulas such as $[Cr(H_2O)_2(en)_2]^{3+}$ and $[Cr(en)_3]^{3+}$. In each of these examples, the coordination number of the Cr^{3+} is 6. In the $[Cr(en)_3]^{3+}$ ion, there are three ethylenediamine ligands that each supply two donor atoms, for a total of 6, and in $[Cr(H_2O)_2(en)_2]^{3+}$, the two ethylenediamine ligands supply a total of 4 donor atoms and the two H_2O molecules supply another 2, so once again the total is 6.

Coordination Number and Geometry

For metal complexes, there are certain geometries that are usually associated with particular coordination numbers.

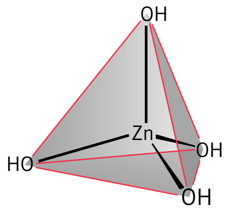
■ Ordinarily, the VSEPR model isn't used to predict the structures of transition metal complexes because it can't be relied on to give correct results when the metal has a partially filled *d* subshell.

Coordination Number 2

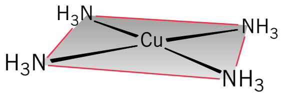
Examples are complexes such as $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$. Usually, these complexes have a linear structure such as

$$[H_3N—Ag—NH_3]^+ \quad \text{and} \quad [NC—Ag—CN]^-$$

(Since the Ag^+ ion has a filled *d* subshell, it behaves as any of the representative elements as far as predicting geometry by VSEPR theory, so these structures are exactly what we would expect based on that theoretical model.)



Tetrahedral
$[Zn(OH)_4]^{2-}$



Square planar
$[Cu(NH_3)_4]^{2+}$

Figure 22.3 | **Tetrahedral and square planar geometries.** These are structures that occur for complexes in which the metal ion has a coordination number of 4. For the copper complex, we are viewing the square planar structure tilted back into the plane of the page.

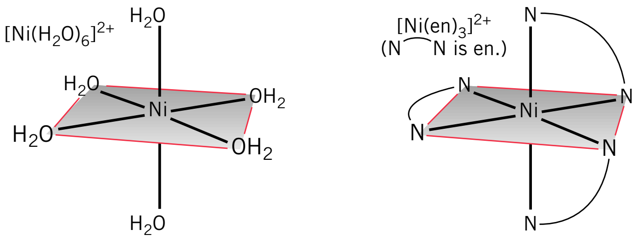
Coordination Number 4

Two common geometries occur when four ligand atoms are bonded to a metal ion—tetrahedral and square planar. These are illustrated in Figure 22.3. The tetrahedral geometry is usually found with metal ions that have completely filled *d* subshells, such as Zn^{2+}. The complexes $[Zn(NH_3)_4]^{2+}$ and $[Zn(OH)_4]^{2-}$ are examples.

Square planar geometries are observed for complexes of Cu^{2+}, Ni^{2+}, Pd^{2+} and especially Pt^{2+}. Examples are $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$, and $[PtCl_4]^{2-}$. The most well-studied square planar complexes are those of Pt^{2+}, because they are considerably more stable than the others.

Coordination Number 6

The most common coordination number for complex ions is 6. Examples are $[Al(H_2O)_6]^{3+}$, $[Co(C_2O_4)_3]^{3-}$, $[Ni(en)_3]^{2+}$, and $[Co(EDTA)]^{-}$. With few exceptions, all complexes with a coordination number of 6 are octahedral. This holds true for those formed from both monodentate and bidentate ligands, as illustrated in Figure 22.4. In describing the shapes of octahedral complexes, most chemists use one of the drawings of the octahedron shown in Figure 22.5. Some common coordination numbers for the metal ions are summarized in Table 22.2.



Complex with monodentate ligands

Complex with bidentate ligands

Figure 22.4 | **Octahedral complexes.** Complexes with this geometry can be formed with either monodentate ligands, such as water, or with polydentate ligands, such as ethylenediamine (en). To simplify the drawing of the ethylenediamine complex, the atoms joining the donor nitrogen atoms in the ligand, $—CH_2—CH_2—$, are represented as the curved line between the N atoms. Also notice that the nitrogen atoms of the bidentate ligand span adjacent positions within the octahedron. This is the case for all polydentate ligands that you will encounter in this book.

Table 22.2 Some Common Coordination Numbers of Metal Ions

Metal Ion	Coordination Number
Al^{3+}	4, 6
Sc^{3+}	6
Ti^{4+}	6
V^{3+}	6
Cr^{3+}	6
Mn^{2+}	6
Fe^{2+}	6
Fe^{3+}	6
Co^{2+}	4, 6
Co^{3+}	6
Ni^{2+}	4, 6
Cu^{+}	2, 4
Cu^{2+}	4, 6
Zn^{2+}	4
Pd^{2+}	4
Ag^{+}	2
Pt^{2+}	4
Pt^{4+}	6
Au^{+}	2, 4
Au^{3+}	4

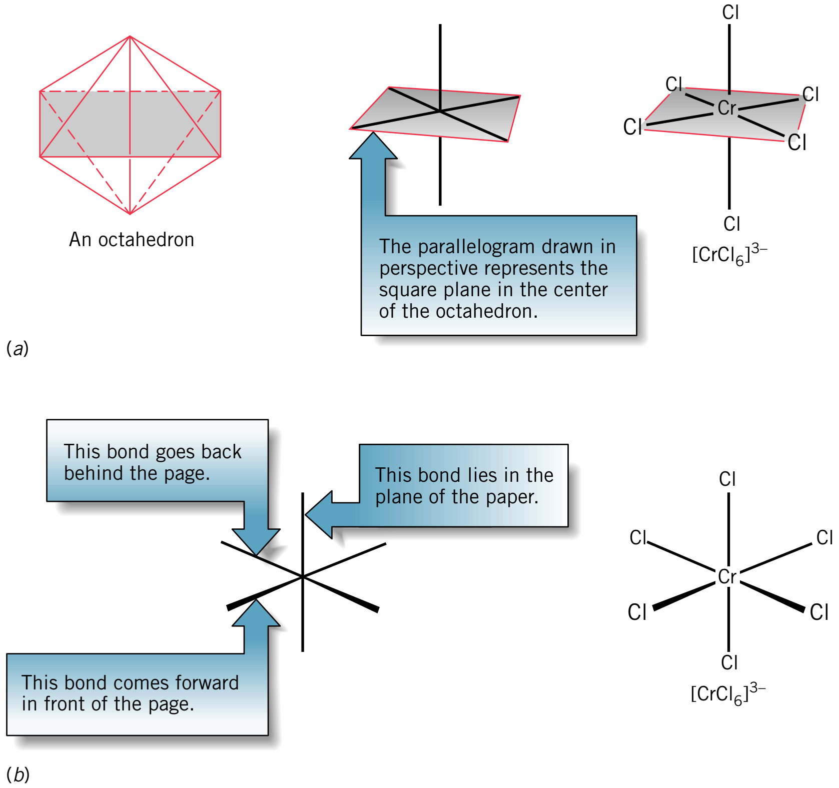

An octahedron
The parallelogram drawn in perspective represents the square plane in the center of the octahedron.
Cl
Cl
Cl
Cr
Cl
Cl
Cl
[CrCl6]3−
(a)
This bond goes back behind the page.
This bond lies in the plane of the paper.
This bond comes forward in front of the page.
Cl
Cl
Cl
Cr
Cl
Cl
Cl
[CrCl6]3−
(b)

Figure 22.5 | **Representations of the octahedral complex, $[CrCl_6]^{3-}$.** (*a*) Drawings similar to those you learned to construct in Chapter 10. (*b*) An alternative method of representing the octahedron.

Practice Exercises

22.6 | What is the coordination number of the metal ion in $[Cr(C_2O_4)_3]^{3-}$? (*Hint*: Identify the ligand and sketch its structure.)

22.7 | What is the coordination number of the metal ion in (a) $[CoCl_2(C_2O_4)_2]^{3-}$, (b) $[Cr(C_2O_4)_2(en)]^{-}$, and (c) $[Co(EDTA)]^{-}$?

22.8 | What is the coordination number of the metal ion in (a) $[PtCl_2(NH_3)_2]$ and (b) $[Ag(S_2O_3)_2]^{3-}$? What are the coordination geometries for the complexes?

22.4 | Isomers of Metal Complexes

When you write the chemical formula for a compound, you might be tempted to think that you should also be able to predict exactly what the structure of the molecule or ion is. As you may realize by now, this just isn't possible in many cases. Sometimes we can use simple rules to make reasonable structural guesses, as in the discussion of the drawing of Lewis structures in Chapter 9, but these rules apply only to simple molecules and ions. For more complex substances, there usually is no way of knowing for sure what the structure of the molecule or ion is without performing the necessary experiments to determine the structure.

One of the reasons that structures can't be predicted with certainty from chemical formulas alone is that there are usually many different ways that the atoms in the formula can be arranged. In fact, it is frequently possible to isolate two or more compounds that actually have the same chemical formula. For example, three different solids, each with its own characteristic color and other properties, can be isolated from a solution of chromium(III) chloride. All three have the same overall composition, and in the absence of other data, their formulas are written $CrCl_3 \cdot 6H_2O$. However, experiments have

Chromium(III) chloride hexahydrate. The hydrated chromium(III) chloride purchased from chemical supply companies is actually $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$. Its green color in both the solid state and solution is due to the complex ion, $[CrCl_2(H_2O)_4]^{+}$. *(Michael Watson)* shown that these solids are actually the salts of three different complex ions. Their actual formulas (and colors) are

$[Cr(H_2O)_6]Cl_3$	purple
$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$	blue-green
$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$	green

Even though their overall compositions are the same, each of these substances is a distinct chemical compound with its own unique set of properties.

The existence of two or more compounds, each having the same chemical formula, is known as **isomerism.** In the preceding example, each salt is said to be an **isomer** of $CrCl_3 \cdot 6H_2O$. For coordination compounds, isomerism can occur in a variety of ways. In the case of $CrCl_3 \cdot 6H_2O$, isomers exist because of the different possible ways that the water molecules and chloride ions can be held in the crystals. In one instance, all of the water molecules serve as ligands, while in the other two, part of the water is present as water of hydration and some of the chloride is bonded to the metal ion. Another example, which is similar in some respects, is $Cr(NH_3)_5SO_4Br$. This "substance" can be isolated as two isomers:

$$[CrSO_4(NH_3)_5]Br \quad \text{and} \quad [CrBr(NH_3)_5]SO_4$$

■ Ag_2SO_4 is soluble but $BaSO_4$ is insoluble.
$BaBr_2$ is soluble but AgBr is insoluble.

They can be distinguished chemically by their differing abilities to react with Ag^+ and Ba^{2+}. The first isomer reacts in aqueous solution with Ag^+ to give a precipitate of AgBr, but it doesn't react with Ba^{2+}. This tells us that Br^- exists as a free ion in the solution. It also suggests that the $SO_4{}^{2-}$ is bound to the chromium and is unavailable to react with Ba^{2+} to give insoluble $BaSO_4$.

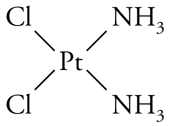
Aqueous solutions of the second isomer, $[CrBr(NH_3)_5]SO_4$, reacts in solution with Ba^{2+} to give a precipitate of $BaSO_4$, which means there is free $SO_4{}^{2-}$ in the solution. There is no reaction with Ag^+, however, because Br^- is bonded to the chromium and is unavailable as free Br^- in the solution. Thus, even though both isomers have the same overall composition, they behave chemically in quite different ways and are therefore distinctly different compounds.

Stereoisomerism

One of the most interesting kinds of isomerism found among coordination compounds is called **stereoisomerism**, which is defined as *differences among isomers that arise as a result of the various possible orientations of their atoms in space.* In other words, when stereoisomerism exists, we have compounds in which the same atoms are attached to each other, but they differ in the way those atoms are arranged in space relative to one another.

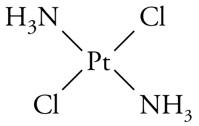
One form of stereoisomerism is called **geometric isomerism**; it is best understood by referring to an example. Consider the square planar complexes having the formula $PtCl_2(NH_3)_2$. There are two ways to arrange the ligands around the platinum, as illustrated below. In one isomer, called the ***cis* isomer**, the chloride ions are *next to each other* and the ammonia molecules are also next to each other. In the other isomer, called the ***trans* isomer**, identical ligands are *opposite each other*. In identifying (and naming) isomers, *cis* means "on the same side," whereas *trans* means "on opposite sides."

■ The isomer on the left, *cis*-$PtCl_2(NH_3)_2$, is the anticancer drug known as *cisplatin*. It is interesting that only the *cis* isomer of this compound is clinically active against tumors. The *trans* isomer is totally ineffective.



cis isomer
cis-diamminedichloroplatinum(II)

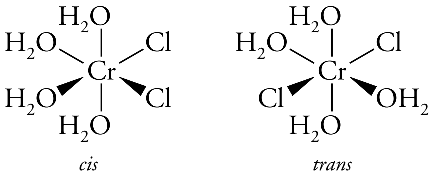
and



trans isomer
trans-diamminedichloroplatinum(II)

Geometric isomerism also occurs for octahedral complexes. For example, consider the ions $[CrCl_2(H_2O)_4]^+$ and $[CrCl_2(en)_2]^+$. Both can be isolated as *cis* and *trans* isomers.

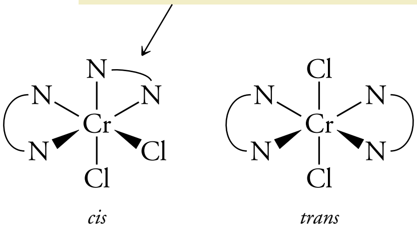
■ The structures of the octahedral complexes are being drawn following the method in Figure 22.5*b*.



cis *trans*

$[CrCl_2(H_2O)_4]^+$

Curved lines connecting nitrogen atoms represent $—CH_2—CH_2—$, which links the nitrogen atoms in ethylenediamine.



cis *trans*

$[CrCl_2(en)_2]^+$

N N is en (ethylenediamine), $NH_2CH_2CH_2NH_2$

In the *cis* isomer, the chloride ligands are both on the same side of the metal ion; in the *trans* isomer, the chloride ligands are on opposite ends of a line that passes through the center of the metal ion.

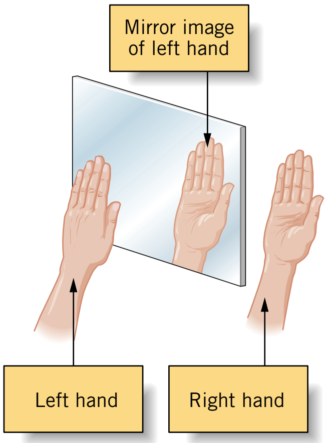
Figure 22.6 | **One difference between left and right hands.** A left-hand glove won't fit the right hand. *(Michael Watson)*

Chirality

There is a second kind of stereoisomerism that is much more subtle than geometric isomerism. This occurs when molecules are exactly the same except for one small difference—they are *nonsuperimposable mirror images of each other*. They bear the same relationship to each other as do your left and right hands. (In fact this relationship between such isomers is sometimes referred to by the term *handedness*.)

Although similar in appearance, your two hands are not exactly alike. If you place one hand over the other, palms down, your thumbs point in opposite directions. **Superimposability** is the ability of two objects to fit "one within the other" with no mismatch of parts. Your left and right hands lack this ability, so we say they are *nonsuperimposable*. This is why your right hand doesn't fit into your left-hand glove (Figure 22.6); your right hand does not match *exactly* the space that corresponds to your left hand.

Your hands are also mirror images of each other. If you hold your left hand so it faces a mirror, and then look at its reflection as illustrated in Figure 22.7, you will see that it looks exactly like your right hand. If it were possible to reach "through the looking glass," your right-hand glove would fit the reflection of your left hand perfectly. Thus, your two hands are *nonsuperimposable mirror images* of each other. If two objects are nonsuperimposable mirror images of each other, they are not identical and are said to be **chiral** or have **chirality**. Your left and right hands have this property and are not exactly alike.



Mirror image of left hand
Left hand
Right hand

Figure 22.7 | **Hands are mirror images of each other.** The image of the left hand reflected in the mirror appears the same as the right hand.

Chiral Complexes with Bidentate Ligands

The most common examples of chirality among coordination compounds occur with octahedral complexes that contain two or three bidentate ligands—for instance, $[CoCl_2(en)_2]^+$ and $[Co(en)_3]^{3+}$. For the complex $[Co(en)_3]^{3+}$, the two nonsuperimposable isomers, called **enantiomers**, are shown in Figure 22.8. For the complex $[CoCl_2(en)_2]^+$, only the *cis* isomer is chiral, as described in Figure 22.9.

■ Chirality is the technical term for "handedness," meaning objects structurally related to each other as are our left and right hands.

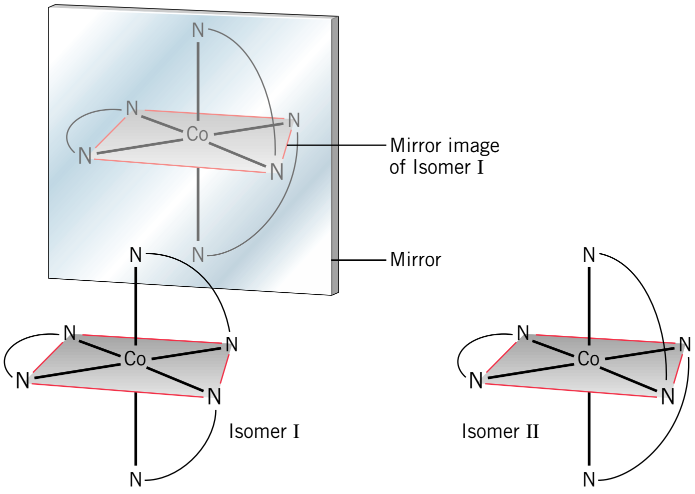
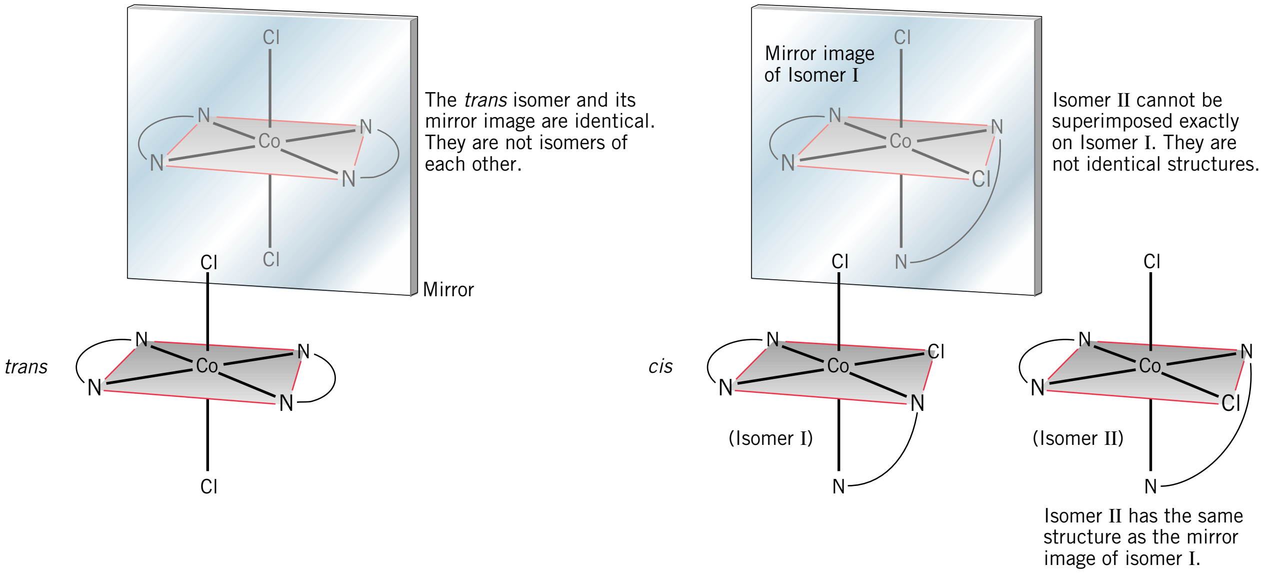


Figure 22.8 | **The two isomers of $[Co(en)_3]^{3+}$.** Isomer II is constructed as the mirror image of isomer I. No matter how Isomer II is turned about, it is not superimposable on Isomer I.

As you can see, chiral isomers differ in only a very minor way from each other. This difference is so subtle that most of their properties are identical. They have identical melting points and boiling points, and in nearly all of their reactions, their behavior is exactly alike. The only way that the difference between chiral molecules or ions manifests itself is in the way that they interact with physical or chemical "probes" that also have a handedness about them. For example, if two reactants are both chiral, then a given isomer of one of them will usually behave slightly differently toward each of the two isomers of the other reactant. This has very profound effects in biochemical reactions, in which many of the molecules involved are chiral.

Optical Isomers

One way that chiral isomers differ is in the way they affect polarized light. Light is *electromagnetic radiation* that possesses both electric and magnetic components that behave like vectors. These vectors oscillate in directions perpendicular to the direction in which the light wave is traveling (Figure 22.10*a*). In ordinary light, the oscillations of the electric and magnetic fields of the photons are oriented randomly around the direction of the light

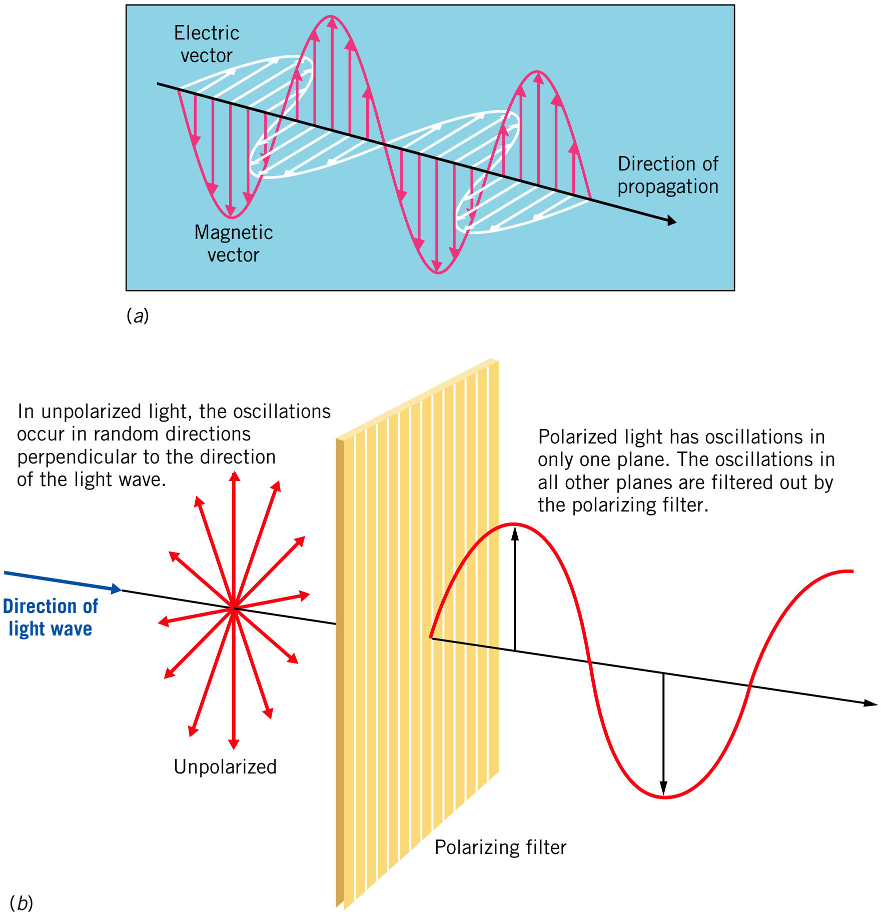


The *trans* isomer and its mirror image are identical. They are not isomers of each other.

Isomer II cannot be superimposed exactly on Isomer I. They are not identical structures.

Isomer II has the same structure as the mirror image of isomer I.

Figure 22.9 | **Isomers of the $[CoCl_2(en)_2]^+$ ion.** The mirror image of the *trans* isomer can be superimposed exactly on the original, so the *trans* isomer is not chiral. The *cis* isomer (Isomer I) is chiral, however, because its mirror image (Isomer II) cannot be superimposed on the original.



In unpolarized light, the oscillations occur in random directions perpendicular to the direction of the light wave.

Polarized light has oscillations in only one plane. The oscillations in all other planes are filtered out by the polarizing filter.

Figure 22.10 | **Unpolarized and polarized light.** (*a*) Light possesses electric and magnetic components that oscillate perpendicular to the direction of the propagation of the light wave. (*b*) In unpolarized light, the electromagnetic oscillations of the photons are oriented at random angles around the axis of the propagation of the light wave. The polarizing filter has the effect of preventing oscillations from passing through unless they are in one particular plane. The result is called plane polarized light.

beam. In **plane-polarized light**, all of the oscillations occur in the same plane (Figure 22.10*b*). Ordinary light can be polarized in several ways. One is to pass it through a special film of plastic, as in a pair of Polaroid sunglasses. This has the effect of filtering out all of the vibrations except those that are in one plane (Figure 22.10*b*).

Chiral isomers like those described in Figures 22.8 and 22.9 have the ability to rotate plane polarized light, as illustrated in Figure 22.11. Because of this phenomenon, chiral isomers are said to be **optical isomers**.

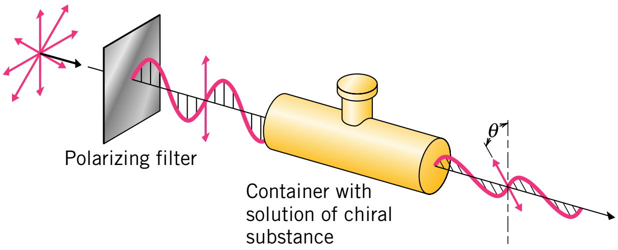


Figure 22.11 | **Rotation of polarized light by a chiral substance.** When plane polarized light passes through a solution of a chiral substance, the plane of polarization is rotated either to the left or to the right. In this illustration, the plane of polarization of the light is rotated to the left (as seen facing the light source).

22.5 | Bonding in Metal Complexes

Complexes of the transition metals differ from the complexes of other metals in two special ways: (1) they are usually colored, whereas complexes of the representative metals are usually (but not always) colorless, and (2) their magnetic properties are often affected by the ligands attached to the metal ion. For example, it is not unusual for a given metal ion to form complexes with different ligands to give a rainbow of colors, as illustrated in Figure 22.12 for a series of complexes of cobalt. Also, because transition metal ions often have incompletely filled *d* subshells, we expect to find many of them with unpaired *d* electrons, and compounds that contain them should be paramagnetic. However, for a given metal ion, the number of unpaired electrons is not always the same from one complex to another. For example, Fe^{2+} has four of its six 3*d* electrons unpaired in the $[Fe(H_2O)_6]^{2+}$ ion, but all of its electrons are paired in the $[Fe(CN)_6]^{4-}$ ion. As a result, the $[Fe(H_2O)_6]^{2+}$ ion is paramagnetic and the $[Fe(CN)_6]^{4-}$ ion is diamagnetic.

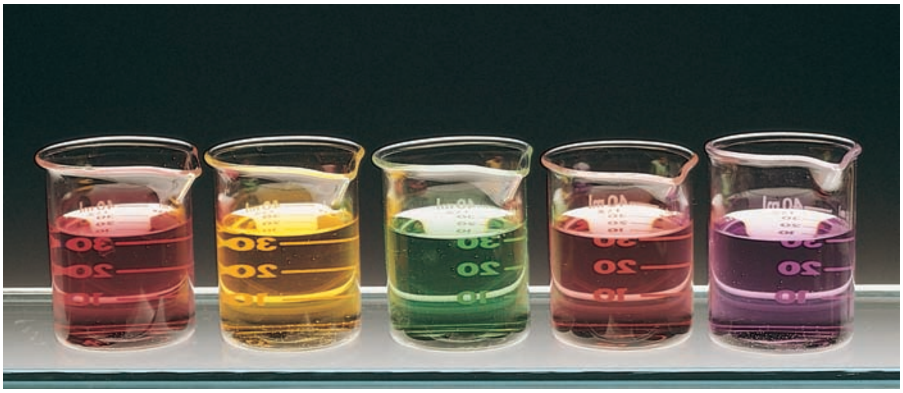


Figure 22.12 | **Colors of complex ions depend on the nature of the ligands.** Each of these brightly colored solutions contains a complex ion of Co^{3+}. The variety of colors arises because of the different ligands (molecules or anions) that are bonded to the cobalt ion in the complexes. *(Michael Watson)*

Crystal Field Theory

Any theory that attempts to explain the bonding in complex ions must also explain their colors and magnetic properties. One of the simplest theories that does this is the **crystal field theory**. This theory gets its name from its original use in explaining the behavior of transition metal ions in crystals. It was discovered later that the theory also works well for transition metal complexes.

■ More complete theories consider the covalent nature of metal–ligand bonding, but crystal field theory nevertheless provides a useful model for explaining the colors and magnetic properties of complexes.

Crystal field theory ignores covalent bonding in complexes. It assumes that the primary stability comes from the electrostatic attractions between the positively charged metal ion and the negative charges of the electrons being donated by the ligands. Crystal field theory's unique approach, though, is the way it examines how the negative charges on the ligands affect the energy of the complex by influencing the energies of the *d* orbitals of the metal ion, and this is what we will focus our attention on here. To understand the theory, therefore, it is essential that you know the shapes and orientation of the *d* orbitals. The *d* orbitals were described in Chapter 8, and they are illustrated again in Figure 22.13.

■ The labels for the *d* orbitals come from the mathematics of quantum mechanics.

First, notice that four of the *d* orbitals have the same shape but point in different directions. These are the $d_{x^2-y^2}$, d_{xy}, d_{xz}, and d_{yz} orbitals. Each has four lobes of electron density. The fifth *d* orbital, labeled d_{z^2}, has two lobes that point in opposite directions along the *z* axis plus a small donut-shaped ring of electron density around the center that is concentrated in the *xy* plane.

Of prime importance to us are the *directions* in which the lobes of the *d* orbitals point. Notice that three of them—d_{xy}, d_{xz}, and d_{yz}—point *between* the *x*, *y*, and *z* axes. The other two—the d_{z^2} and $d_{x^2-y^2}$ orbitals—have their maximum electron densities *along* the *x*, *y*, and *z* axes.

Now let's consider constructing an octahedral complex within this coordinate system. We can do this by bringing ligands in along each of the axes as shown in Figure 22.14. The question we want to answer is: How do these ligands affect the energies of the *d* orbitals?

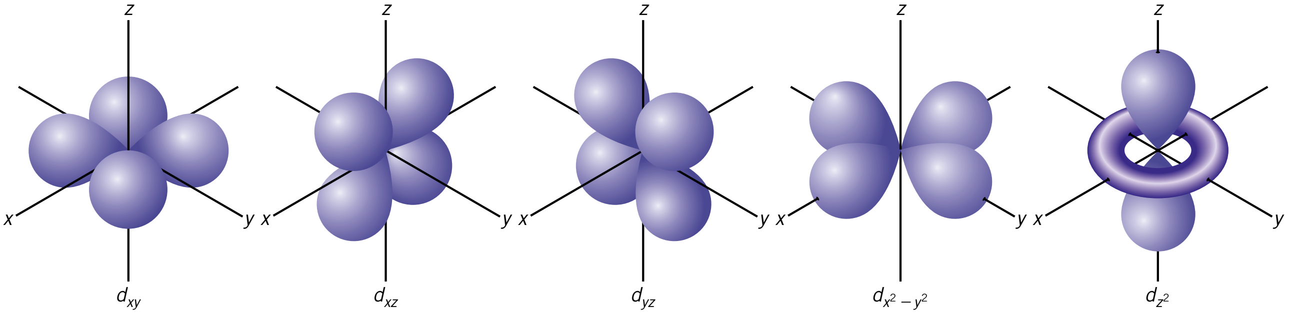


Figure 22.13 | **The shapes and directional properties of the five *d* orbitals of a *d* subshell.**

In an isolated atom or ion, all of the *d* orbitals of a given *d* subshell have the same energy. Therefore, an electron will have the same energy regardless of which *d* orbital it occupies. In an octahedral complex, however, this is no longer true. If the electron is in the $d_{x^2-y^2}$ or d_{z^2} orbital, it is forced to be nearer the negative charge of the ligands than if it is in a d_{xy}, d_{xz}, or d_{yz} orbital. Since the electron itself is negatively charged and is repelled by the charges of the ligands, the electron's potential energy will be higher in the $d_{x^2-y^2}$ and d_{z^2} orbitals than in a d_{xy}, d_{xz}, or d_{yz} orbital. Therefore, as the complex is formed, the *d* subshell actually splits into *two* new energy levels, as shown in Figure 22.15. Here we see that regardless of which orbital the electron occupies, its energy increases because it is repelled by the negative charges of the approaching ligands. However, the electron is repelled *more* (and has a higher energy) if it is in an orbital that points directly at the ligands than if it occupies an orbital that points between them.

In an octahedral complex, the energy difference between the two sets of *d*-orbital energy levels is called the **crystal field splitting**. It is usually given the symbol Δ (delta), and its magnitude depends on the following factors:

The nature of the ligand. *Some ligands produce a larger splitting of the energies of the d orbitals than others.* For a given metal ion, for example, cyanide always gives a large value of Δ and F^- always gives a small value. We will have more to say about this later.

The oxidation state of the metal. *For a given metal and ligand, the size of Δ increases with an increase in the oxidation number of the metal.* As electrons are removed from a metal and the charge on the ion becomes more positive, the ion becomes smaller. This means that the ligands are attracted to the metal more strongly and they can approach the center of the complex more closely. As a result, they also approach the *d* orbitals along the *x*, *y*, and *z* axes more closely, and thereby cause a greater repulsion. This causes a greater splitting of the two *d*-orbital energy levels and a larger value of Δ.

The row in which the metal occurs in the periodic table. *For a given ligand and oxidation state, the size of Δ increases going down a group.* In other words, for a given ligand, an ion of an element in the first row of transition elements has a smaller value of Δ than the ion of a heavier member of the same group. Thus, comparing complexes of Ni^{2+} and Pt^{2+} with the same ligand, we find that the platinum complex has the larger crystal field splitting. The explanation of this is that in the larger ion (e.g., Pt^{2+}), the *d* orbitals are larger and more diffuse and extend farther from the nucleus in the direction of the ligands. This produces a larger repulsion between the ligands and the orbitals that point at them.

The magnitude of Δ is very important in determining the properties of complexes, including the stabilities of oxidation states of the metal ions, the colors of complexes, and their magnetic properties. Let's look at some examples.

TOOLS

Crystal field splitting pattern for octahedral complexes

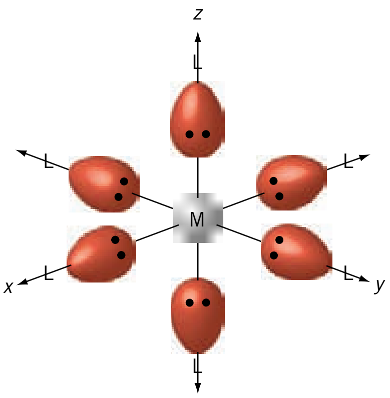


Figure 22.14 | **An octahedral complex ion with ligands that lie along the *x*, *y*, and *z* axes.** The dots represent the lone electron pairs on the ligands, which are oriented so that they point at the metal ion.

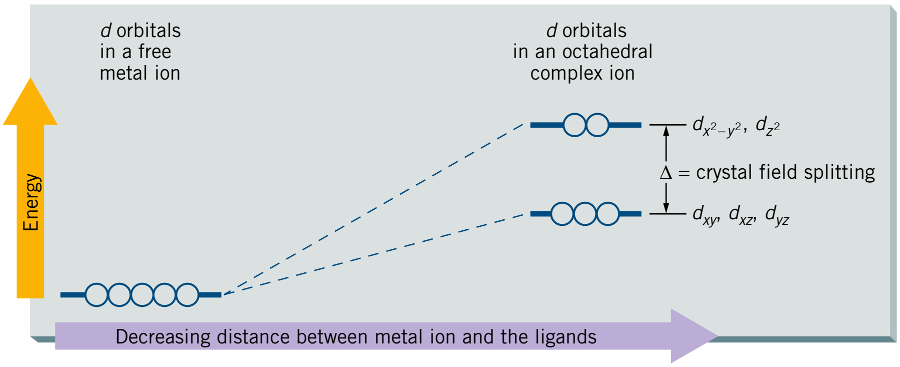

d orbitals
in a free
metal ion
d orbitals
in an octahedral
complex ion
$d_{x^2-y^2}$, d_{z^2}
Δ = crystal field splitting
d_{xy}, d_{xz}, d_{yz}
Energy
Decreasing distance between metal ion and the ligands

Figure 22.15 | **The changes in the energies of the *d* orbitals of a metal ion as an octahedral complex is formed.** As the ligands approach the metal ion, the *d* orbitals split into two new energy levels.

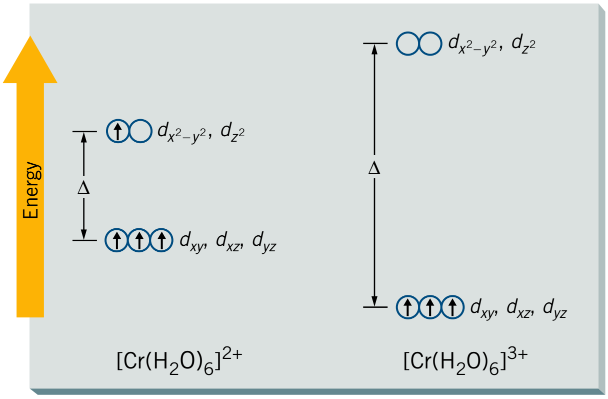


Figure 22.16 | **Energy level diagrams for the $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ ions.** The magnitude of Δ is larger for the chromium(III) complex because the Cr^{3+} ion is smaller than the Cr^{2+} ion and the ligands are drawn closer to the metal ion, thereby increasing repulsions felt by the $d_{x^2-y^2}$ and d_{z^2} orbitals.

Stabilities of Oxidation States

Comparing the cations formed by chromium, it is found that the Cr^{2+} ion is very easily oxidized to Cr^{3+}. This can be explained by crystal field theory. In water, we expect these ions to exist as the complexes $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$, respectively. Let's examine the energies and electron populations of the *d*-orbital energy levels in each complex (Figure 22.16).

The element chromium has the electron configuration

$$\text{Cr} \qquad [\text{Ar}]\ 3d^5 4s^1$$

Removing two electrons gives the Cr^{2+} ion, and removing three gives Cr^{3+}:

$$\text{Cr}^{2+} \qquad [\text{Ar}]\ 3d^4$$
$$\text{Cr}^{3+} \qquad [\text{Ar}]\ 3d^3$$

Next, we distribute the *d* electrons among the various *d* orbitals following Hund's rule, but for Cr^{2+} we have to make a choice. Should the electrons all be forced into the lower of the two energy levels, or should they be spread out? From the diagram we see that the fourth electron does not pair with one of the others in the lower energy *d*-orbital level. Instead, three electrons go into the lower level and the fourth is in the upper level. We will discuss *why* this happens later, but for now, let's use the two energy diagrams to explain why Cr^{2+} is so easy to oxidize.

There are actually two factors that favor the oxidation of Cr(II) to Cr(III). First, the electron that is removed from Cr^{2+} to give Cr^{3+} comes from the *higher* energy level, so oxidizing the chromium(II) *removes* a high-energy electron. The second factor is the effect caused by increasing the oxidation state of the chromium. As we've pointed out, this increases the magnitude of Δ, and as you can see, the energy of the three electrons that remain is lowered. Thus, both the removal of a high-energy electron and the lowering of the energy of the electrons that are left behind help make the oxidation occur, so the $[Cr(H_2O)_6]^{2+}$ ion is very easily oxidized to $[Cr(H_2O)_6]^{3+}$.

Colors of Metal Complexes

When light is absorbed by an atom, molecule, or ion, the energy of the photon raises an electron from one energy level to another. In many substances, such as sodium chloride, the energy difference between the highest energy populated level and the lowest energy unpopulated level is quite large, so the frequency of a photon that carries the necessary energy lies outside the visible region of the spectrum. The substance appears white because visible light is unaffected; it is reflected unchanged.

■ Remember, $E = h\nu$. The energy of the photon absorbed determines the frequency (and wavelength) of the absorbed light.

For complex ions of the transition metals, the energy difference between the *d*-orbital energy levels is not very large, and photons with frequencies in the visible region of the spectrum are able to raise an electron from the lower-energy set of *d* orbitals to the higher-energy set. This is shown in Figure 22.17 for the $[Cr(H_2O)_6]^{3+}$ ion.

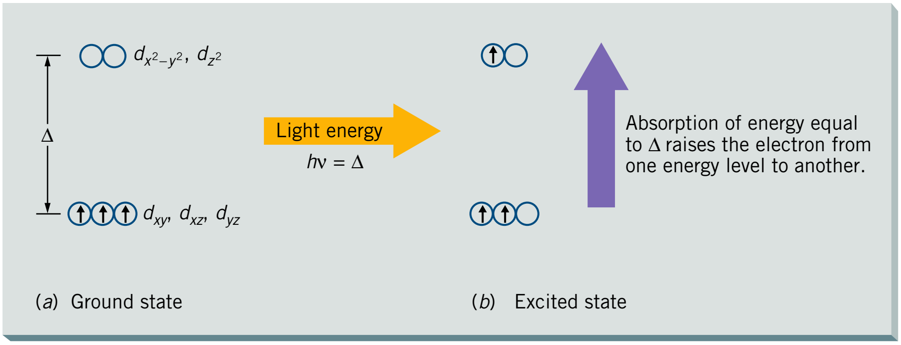

$d_{x^2-y^2}$, d_{z^2}
Δ
d_{xy}, d_{xz}, d_{yz}
Light energy
$h\nu$ = Δ
Absorption of energy equal to Δ raises the electron from one energy level to another.
(a) Ground state
(b) Excited state

Figure 22.17 | **Absorption of a photon by the $[Cr(H_2O)_6]^{3+}$ complex.** (*a*) The electron distribution in the ground state of the $[Cr(H_2O)_6]^{3+}$ ion. (*b*) Light energy raises an electron from the lower energy set of *d* orbitals to the higher energy set.

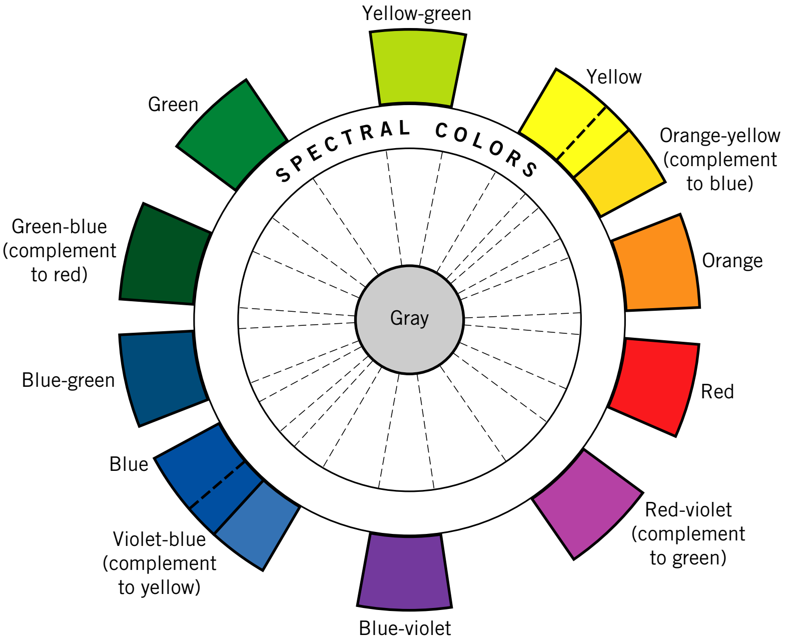

Yellow-green
Yellow
Orange-yellow (complement to blue)
Orange
Red
Red-violet (complement to green)
Blue-violet
Violet-blue (complement to yellow)
Blue
Blue-green
Green-blue (complement to red)
Green
SPECTRAL COLORS
Gray

Figure 22.18 | **A color wheel.** Colors that are across from each other are called complementary colors. When a substance absorbs a particular color, light that is reflected or transmitted has the color of its complement. Thus, something that absorbs red light appears green-blue, and vice versa.

As you know, white light contains photons of all of the frequencies and colors in the visible spectrum. If we shine white light through a solution of a complex, the light that passes through has all of the colors *except* those that have been absorbed. It is not difficult to determine what will be seen if we know what colors are being absorbed. All we need is a color wheel like the one shown in Figure 22.18. Across from each other on the color wheel are ***complementary colors***. Green-blue is the complementary color to red, and yellow is the complementary color to violet-blue. If a substance absorbs a particular color when bathed in white light, the perceived color of the reflected or transmitted light is the complementary color. In the case of the $[Cr(H_2O)_6]^{3+}$ ion, the light absorbed when the electron is raised from one set of *d* orbitals to the other has a frequency of 5.22×10^{14} Hz, which is the color of yellow light. This is why a solution of this ion appears violet.[4] An instrument that measures the wavelength of light and the amount of light absorbed by a compound is a spectrophotometer (shown in Figure 22.19).

Because of the relationship between the energy and the frequency of light, we see that the color of the light absorbed by a complex depends on the magnitude of Δ; the larger the size of Δ, the more energy the photon must have and the higher will be the frequency of the absorbed light. For a given metal in a given oxidation state, the size of Δ depends on the ligand. Some ligands give a large crystal field splitting, while others give a small splitting. For example, ammonia produces a larger splitting than water, so the complex $[Cr(NH_3)_6]^{3+}$ absorbs light of higher energy and higher frequency than $[Cr(H_2O)_6]^{3+}$. (The $[Cr(NH_3)_6]^{3+}$ absorbs blue light and appears yellow.) Because changing the ligand changes Δ, the same metal ion is able to form a variety of complexes with a large range of colors.

Figure 22.19 | **A spectrophotometer typically found in an undergraduate teaching laboratory.**

A ligand that produces a large crystal field splitting with one metal ion also produces a large Δ in complexes with other metals. For example, cyanide ion is a very effective ligand and always gives a very large Δ, regardless of the metal to which it is bound. Ammonia is less effective than cyanide ion but more effective than water. Thus, ligands can be arranged

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[4] The perception of color is actually somewhat more complex than this because of the varying sensitivity of the human eye to various wavelengths. For example, the eye is much more sensitive to green than to red. If a compound reflects both of these colors with equal intensity, it will appear greenish simply because the eye sees green better than it sees red.

■ The order of the ligands can be determined by measuring the frequencies of the light absorbed by complexes.

TOOLS Spectrochemical series

in order of their effectiveness at producing a large crystal field splitting. This sequence is called the **spectrochemical series.** Such a series containing some common ligands arranged in order of their decreasing strength is

$$CN^- > NO_2^- > en > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$$

For a given metal ion, cyanide ion produces the largest Δ and iodide produces the smallest.

Magnetic Properties of Complexes

Let's return to the question of the electron distribution among the *d* orbitals in Cr^{2+} complexes. As you saw above, this ion has four *d* electrons, and we noted that in placing these electrons in the *d* orbitals, we had to make a decision about where to place the fourth electron. There's no question about the fate of the first three. They just spread out across the three *d* orbitals in the lower level with their spins unpaired. In other words, we just follow Hund's rule, which we learned to apply in Chapter 8. However, when we come to the fourth electron we have to decide whether to pair it with one of the electrons already in a *d* orbital of the lower set or to place it in one of the *d* orbitals of the higher set.[5] If we place it in the lower energy level, we give it extra stability (lower energy), but some of this stability is lost because it requires energy, called the **pairing energy**, *P*, to force the electron into an orbital that's already occupied by an electron. On the other hand, if we place it in the higher level, we are relieved of the burden of pairing the electron, but it also tends to give the electron a higher energy. Thus, for the fourth electron, "pairing" and "placing" affect the energy of the complex in opposite ways.

The critical factor in determining whether the fourth electron enters the lower level and becomes paired, or whether it enters the higher level with the same spin as the other *d* electrons, is the magnitude of Δ. If Δ is larger than the pairing energy *P*, then greater stability is achieved if the fourth electron is paired with one in the lower level. If Δ is small compared to *P*, then greater stability is obtained by spreading the electrons out as much as possible. The complexes $[Cr(H_2O)_6]^{2+}$ and $[Cr(CN)_6]^{4-}$ illustrate this well.

Water is a ligand that does not produce a large Δ, so $P > \Delta$, and minimum pairing of the electrons takes place. This explains the energy level diagram for the $[Cr(H_2O)_6]^{2+}$ complex in Figure 22.20*a*. When cyanide is the ligand, however, a very large Δ is obtained, and this leads to pairing of the fourth electron with one in the lower set of *d* orbitals. This is shown in Figure 22.20*b*. By measuring the degree of paramagnetism of the two complexes, it can be demonstrated experimentally that $[Cr(H_2O)_6]^{2+}$ has four unpaired electrons and the $[Cr(CN)_6]^{4-}$ ion has just two.

For octahedral chromium(II) complexes, there are two possibilities in terms of the number of unpaired electrons. They contain either four or two, depending on the magnitude of Δ. When there is the maximum number of unpaired electrons, the complex is described as being **high-spin**; when there is the minimum number of unpaired electrons it is described as being **low-spin**. High- and low-spin octahedral complexes are possible

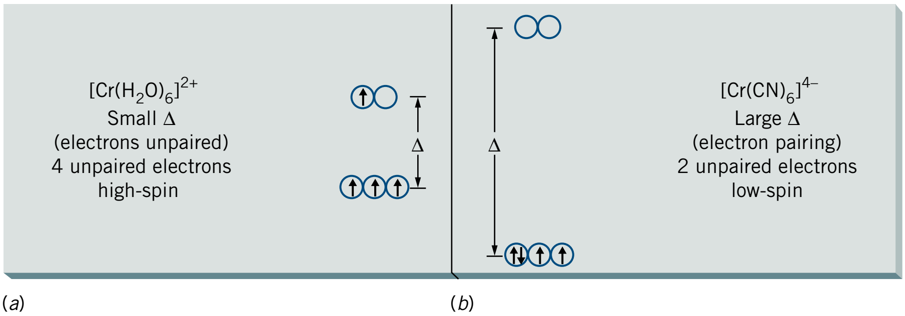

Figure 22.20 | **The effect of Δ on the electron distribution in a complex with four *d* electrons.** (*a*) When Δ is small, the electrons remain unpaired. (*b*) When Δ is large, the lower energy level accepts all four electrons and two electrons become paired.

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[5] We've never had to make this kind of decision before because the energy levels in atoms were always widely spaced. In complex ions, however, the spacing between the two *d*-orbital energy levels is fairly small.

when the metal has a d^4, d^5, d^6, or d^7 electron configuration. Let's look at another example—one containing the Fe^{2+} ion, which has the electron configuration,

$$Fe^{2+} \qquad [Ar]\ 3d^6$$

At the beginning of this section we mentioned that the $[Fe(H_2O)_6]^{2+}$ ion is paramagnetic and has four unpaired electrons, while the $[Fe(CN)_6]^{4-}$ ion is diamagnetic, meaning it has no unpaired electrons. Now we can see why, by referring to Figure 22.21. Water produces a weak splitting and a minimum amount of pairing of electrons. When the six *d* electrons in the Fe^{2+} ion are distributed, one must be paired in the lower level after filling the upper level. The result is four unpaired *d* electrons, and a high-spin complex. Cyanide ion, however, produces a large splitting, so $\Delta > P$. This means that maximum pairing of electrons in the lower level takes place, and a low-spin complex is formed. Six electrons are just the right amount to completely fill all three of these *d* orbitals, and since all of the electrons are paired, the complex is diamagnetic.

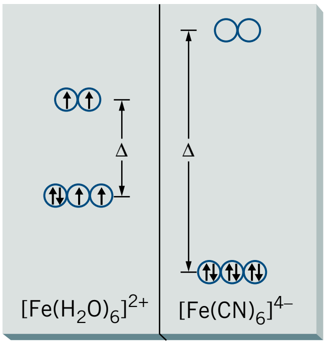


Figure 22.21 | **The distribution of *d* electrons in $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$.** The magnitude of Δ for the cyanide complex is much larger than for the water complex. This produces a maximum pairing of electrons in the lower energy set of *d* orbitals in $[Fe(CN)_6]^{4-}$.

Crystal Field Theory and Other Geometries

The crystal field theory can be extended to geometries other than octahedral. The effect that changing the structure of the complex has on the energies of the *d* orbitals is to change the splitting pattern.

Square Planar Complexes

We can form a square planar complex from an octahedral one by removing the ligands that lie along the *z* axis. As this happens, the ligands in the *xy* plane are able to approach the metal a little closer because they are no longer being repelled by ligands along the *z* axis. The effect of these changes on the energies of the *d* orbitals is illustrated in Figure 22.22.

■ In Figure 22.22, as the energies of the *d* orbitals change, the d_{z^2} orbital drops in energy by the same amount as the $d_{x^2-y^2}$ rises. Similarly, the energies of the d_{xz} and d_{yz} orbitals drop only half as much as the energy of the d_{yz} rises. In this way, if all the *d* orbitals were filled, the changes in geometry would have no effect on the total energy of the complex.

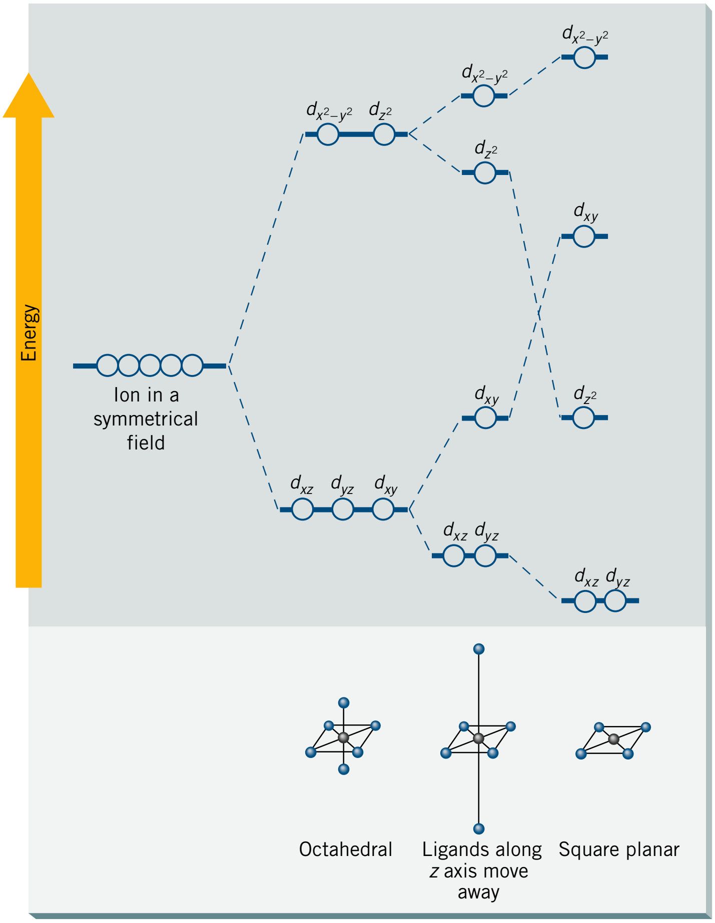


Figure 22.22 | **Energies of *d* orbitals in complexes with various structures.** The splitting pattern of the *d* orbitals changes as the geometry of the complex changes.

The repulsions felt by the *d* orbitals that point in the *z* direction are reduced, so we find that the energies of the d_{z^2}, d_{xz}, and d_{yz} orbitals drop. At the same time, the energies of the orbitals in the *xy* plane feel greater repulsions, so the $d_{x^2-y^2}$ and d_{xy} rise in energy.

Nickel(II) ion (which has eight *d* electrons) forms a complex with cyanide ion that is square planar and diamagnetic. In this complex the strong field produced by the cyanide ions yields a large energy separation between the d_{xy} and $d_{x^2-y^2}$ orbitals, so that a low-spin complex results. The electron distribution in this complex is illustrated in Figure 22.23.

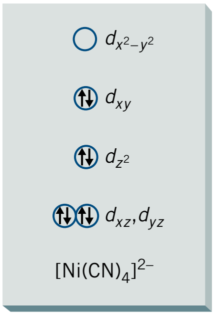


Figure 22.23 | **Distribution of the electrons among the *d* orbitals of nickel in the diamagnetic $[Ni(CN)_4]^{2-}$ ion.**

Tetrahedral Complexes

The splitting pattern for the *d* orbitals in a tetrahedral complex is illustrated in Figure 22.24. Now, the ligands are approaching the metal center between the axes, so the order of the energy levels is exactly opposite to that in an octahedral complex. In addition, the size of the crystal field splitting, Δ, is also much smaller for a tetrahedral complex than for an octahedral one. (Actually, $\Delta_{tet} \approx \frac{4}{9}\Delta_{oct}$ for the same metal ion with the same ligands.) This small Δ is always less than the pairing energy, so tetrahedral complexes are always high-spin complexes.

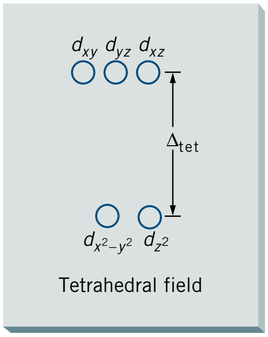


Figure 22.24 | **Splitting pattern of the *d* orbitals for a tetrahedral complex.** The crystal field splitting for the tetrahedral structure (Δ_{tet}) is smaller than that for the octahedral structure (Δ_{oct}). For complexes with the same ligands, $\Delta_{tet} \approx \frac{4}{9}\Delta_{oct}$.

22.6 | Biological Functions of Metal Ions

Most of the compounds in our bodies have structures based on carbon as the principal element, and their functions are usually related to the geometries assumed by carbon-containing compounds, as well as the breaking and forming of carbon–carbon, carbon–hydrogen, carbon–oxygen, and carbon–nitrogen bonds. In Chapter 23 we will discuss some classes of biochemical molecules.

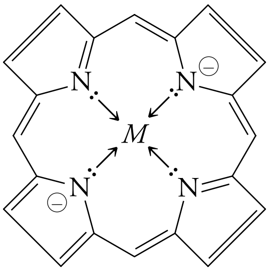
Our bodies also require certain metal ions in order to operate, and without them life cannot be sustained. For this reason, the study of metals in biological systems has become a very important branch of biochemistry, and a large number of research papers are published annually that deal with this topic. Table 22.3 lists some of the essential metals and the functions fulfilled by their ions.

A few metals, such as sodium and potassium, are found as simple monatomic ions in body fluids. Most metal ions, however, become bound by ligands and do their work as part of metal complexes. As examples, we will look briefly at two metals—iron and cobalt.

Table 22.3 Some Biologically Important Metals and the Corresponding Human Body Functions with which Their Ions Are Involved

Metal	Body Function
Na, Ca	Blood pressure and blood coagulation
Fe	Oxygen transport and storage
Ca	Teeth and bone formation
Ca	Urinary stone formation
Zn	Control of pH in blood
Ca, Mg	Muscle contraction
K	Maintenance of stomach acidity
Fe, Cu	Respiration
Cu	Bone health
Ca, Fe, Co	Cell division

Iron is one of the essential elements required by our bodies. We obtain it in a variety of ways in our diets. Iron is involved in oxygen transport in our blood and in retaining oxygen in muscle tissue so that it's available when needed. The iron is present as Fe^{2+} held in a complex in which the basic ligand structure is



This ligand composition, with its square planar arrangement of nitrogen atoms that bind to a metal ion, is called a *porphyrin structure.* It is the ligand structure in a biologically active unit called heme. Heme is the oxygen-carrying component of the blood protein hemoglobin and in myoglobin, which is found in muscle tissue.

In the lungs, O_2 molecules are absorbed by the blood and become bound to Fe^{2+} ions in the heme units of hemoglobin (Figure 22.25). Blood circulation then carries the O_2 to tissues where it is needed, at which time it is released by the Fe^{2+}. One of the important functions of the porphyrin ligand in this process is to prevent the Fe^{2+} from being oxidized by the O_2. (In fact, if the iron is oxidized to Fe^{3+}, it is no longer able to carry O_2.) In muscle tissue, heme units in the protein myoglobin take O_2 from hemoglobin and hold it until it's needed. In this way, muscle tissue is able to store O_2 so that plenty of it is available when the muscle must work hard.

Heme units are also present in proteins called cytochromes, where the iron is involved in electron transfer reactions that employ the +2 and +3 oxidation states of iron.

- The porphyrin structure is present in chlorophyll too, where the metal bound in the center is Mg^{2+}. Chlorophyll absorbs sunlight (solar energy) which is used by plants to convert carbon dioxide and water into glucose and oxygen.

- The iron in hemoglobin also binds CO_2 and helps transport it back to the lungs to be exhaled.

- The ability of transition metals to exist in different oxidation states is one reason they are used in biological systems. They can easily take part in oxidation–reduction reactions. Copper(I) and copper(II) ions constitute another pair involved in catalyzing biochemical redox reactions.

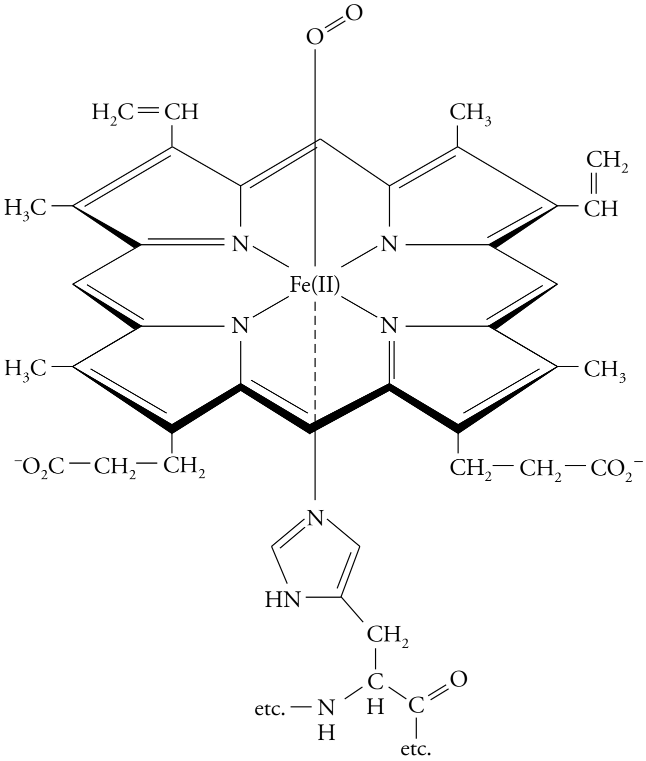
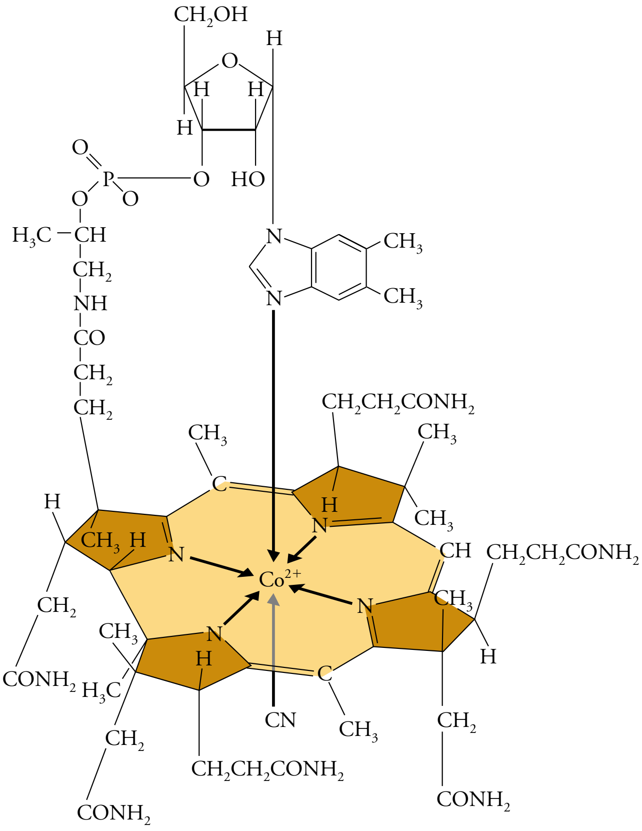


Figure 22.25 | **Iron(II) bound to oxygen in heme.** The porphyrin ring ligand in heme surrounds an Fe^{2+} ion that binds an O_2 molecule. In its oxygenated form, the Fe^{2+} is octahedrally coordinated in the structure.

Figure 22.26 | **The structure of cyanocobalamin.** Notice the cobalt ion in the center of the square planar arrangement of nitrogen atoms that are part of the ligand structure. Overall, the cobalt is surrounded octahedrally by donor atoms.



Vitamin B_{12}

A structure similar to heme is found in cyanocobalamin, the form of vitamin B_{12} found in vitamin pills (Figure 22.26). Here, a Co^{2+} ion is held in a square planar ligand structure (called a *corrin ring*) that is slightly different from that found in heme. Certain enzymes (biological catalysts) require cobalamins to function. Vitamin B_{12} is essential in our diets, and a deficiency in this vitamin leads to a disease called pernicious anemia.

We have illustrated here just a few examples of the important roles that metal ions play in living systems. They are roles that cannot be fulfilled by other carbon-based compounds, some of which are described in Chapter 23.

Summary

Complex Ions of Metals. **Coordination compounds** contain **complex ions** (also called **complexes** or **coordination complexes**), formed from a metal ion and a number of ligands. **Ligands** are Lewis bases and may be **monodentate**, **bidentate**, or, in general, **polydentate**, depending on the number of **donor atoms** that they contain. Water is the most common monodentate ligand. Polydentate ligands bind to a metal through two or more donor atoms and yield ring structures called **chelates**. Common bidentate ligands are oxalate ion and ethylenediamine (en); a common polydentate ligand is ethylenediaminetetraacetic acid (EDTA), which has six donor atoms.

In the formula of a complex, the metal is written first, followed by the formulas of the ligands (anions first, in alphabetical order, followed by neutral ligands, in alphabetical order). Brackets are used to enclose the set of atoms that make up the complex, with the charge on the complex written outside the brackets. The charge on the complex is the algebraic sum of the charges on the metal ion and the charges on the ligands.

Complexes of polydentate ligands are more stable than similar complexes formed with monodentate ligands, partly because a polydentate ligand is less likely to be lost completely if one of its donor atoms becomes detached from the metal ion. The larger positive entropy change for the dissociation of complexes with monodentate ligands also favors their dissociation compared with complexes of polydentate ligands. The phenomenon is called the **chelate effect**.

Nomenclature of Complexes. Complexes are named following a set of rules developed by the IUPAC. These are summarized on pages 1023 to 1024.

Coordination Number and Structure. The **coordination number** of a metal ion in a complex is the number of donor atoms attached to the metal ion. Polydentate ligands supply two or more donor atoms, which must be taken into account when determining the coordination number from the formula of the complex. Geometries associated with common coordination numbers are as follows: for coordination number 2, linear; for coordination number 4, tetrahedral and square planar (especially for Pt^{2+} complexes); and for coordination number 6, octahedral.

Isomers of Coordination Compounds. When two or more distinct compounds have the same chemical formula, they are **isomers** of each other. **Stereoisomers** have the same atoms attached to each other, but the atoms are arranged differently in space. In a ***cis* isomer**, attached groups of atoms are on the same side of some reference plane through the molecule. In a ***trans* isomer**, they are on opposite sides. *Cis* and *trans* isomerism is a form of **geometric isomerism. Chiral** isomers are exactly the same in every way but one—they are not superimposable on their mirror images. These kinds of isomers exist for complexes of the type $M(AA)_3$, where M is a metal ion and AA is a bidentate ligand, and also for complexes of the type *cis*-$M(AA)_2a_2$, where a is a monodentate ligand. Chiral isomers that are mirror images of each other are said to be **enantiomers**. Because they are able to rotate **plane-polarized light**, they are called **optical isomers**.

Crystal Field Theory. In an octahedral complex, the ligands influence the energies of the d orbitals by splitting the d subshell into two energy sublevels. The lower-energy one consists of the d_{xy}, d_{xz}, and d_{yz} orbitals; the higher-energy level consists of the d_{z^2} and $d_{x^2-y^2}$ orbitals. The energy difference between the two new d sublevels is the **crystal field splitting**, Δ, and for a given ligand it increases with an increase in the oxidation state of the metal and it depends on the period number in which the metal is found. For a given metal ion, Δ depends on the ligand.

In the **spectrochemical series**, ligands are arranged in order of their ability to cause a large Δ. Cyanide ion produces the largest crystal field splitting, whereas iodide ion produces the smallest. **Low-spin** complexes result when Δ is larger than the **pairing energy**—the energy needed to cause two electrons to become paired in the same orbital. **High-spin** complexes occur when Δ is smaller than the pairing energy. Light of energy equal to Δ is absorbed when an electron is raised from the lower-energy set of d orbitals to the higher set, and the color of the complex is determined by the colors that remain in the transmitted light. Crystal field theory can also explain the relative stabilities of oxidation states, in many cases.

Different splitting patterns of the d orbitals occur for other geometries. The patterns for square planar and tetrahedral geometries are described in Figures 22.22 and 22.24, respectively. The value of Δ for a tetrahedral complex is only about 4/9 that of Δ for an octahedral complex.

Metals in Living Systems. Most metals required by living organisms perform their actions when bound as complex ions. Heme contains Fe^{2+} held in a square planar porphyrin ligand and binds to O_2 in hemoglobin and myoglobin. Heme is also found in cytochromes, where it participates in redox reactions involving Fe^{2+} and Fe^{3+}. Vitamin B_{12}, required by the body to prevent the vitamin deficiency disease called pernicious anemia, contains Co^{2+} in a corrin ring structure, which is similar to the porphyrin ring.

Tools for Problem Solving

The following tools were introduced in this chapter. Study them carefully so you can select the appropriate tool when needed.

Rules for writing formulas for complexes (page 1020)

The following rules apply whenever you have to write the formula for a complex ion:

1. The symbol for the metal ion is always given first, followed by the ligands.
2. When more than one kind of ligand is present, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order).
3. The charge on the complex is the algebraic sum of the charge on the metal ion and the charges on the ligands.

Rules for naming complexes (pages 1023 to 1024)

Naming complexes follows rules that are an extension of the rules you learned earlier. You have to learn them and then apply them when you have to name a complex or write a formula given the name.

Crystal field splitting pattern for octahedral complexes (page 1033)

Figure 22.15 forms the basis for applying the principles of crystal field theory to octahedral complexes. To use it, you need the electron configuration of the metal ion. First, write the electron configuration for the metal under consideration. Then, remove electrons from the atom starting with the outer *s* subshell first, followed if necessary by electrons from the underlying *d* subshell. For a complex under consideration, set up the splitting diagram and place electrons into the *d* orbitals following Hund's rule. For d^4, d^5, d^6, and d^7 configurations, you may have to decide whether a high- or low-spin configuration is preferred.

Spectrochemical series (page 1036)

Use the location of ligands in the spectrochemical series to compare their effects on the crystal field splitting. The series is

$$\mathrm{CN^-} > \mathrm{NO_2^-} > \mathrm{en} > \mathrm{NH_3} > \mathrm{H_2O} > \mathrm{C_2O_4^{2-}} > \mathrm{OH^-} > \mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$$

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Complex Ions

22.1 The formation of the complex ion $[\mathrm{Cu(H_2O)_6}]^{2+}$ is described as a Lewis acid–base reaction. Explain.

- **(a)** What are the formulas of the Lewis acid and the Lewis base in this reaction?
- **(b)** What is the formula of the ligand?
- **(c)** What is the name of the species that provides the donor atom?
- **(d)** What atom is the donor atom, and why is it so designated?
- **(e)** What is the name of the species that is the acceptor?

22.2 To be a ligand, a substance should also be a Lewis base. Explain.

22.3 Why are substances that contain complex ions often called coordination compounds?

22.4 Use Lewis structures to diagram the formation of $\mathrm{Cu(NH_3)_4}^{2+}$ and $\mathrm{CuCl_4}^{2-}$ ions from their respective components.

22.5 What must be true about the structure of a ligand classified as *bidentate*?

22.6 What is a *chelate*? Use Lewis structures to diagram the way that the oxalate ion, $\mathrm{C_2O_4}^{2-}$, functions as a chelating agent.

22.7 How many donor atoms does EDTA^{4-} have?

22.8 Explain how a salt of EDTA^{4-} can retard the spoilage of salad dressing.

22.9 How does a salt of EDTA^{4-} in shampoo make the shampoo work better in hard water?

22.10 The cobalt(III) ion, Co^{3+}, forms a 1:1 complex with EDTA^{4-}. What is the net charge, if any, on this complex, and what would be a suitable formula for it (using the symbol EDTA)?

22.11 Which complex is more stable, $[\mathrm{Cr(NH_3)_6}]^{3+}$ or $[\mathrm{Cr(en)_3}]^{3+}$? Why?

Coordination Number and Structure

22.12 What is a *coordination number*? What structures are generally observed for complexes in which the central metal ion has a coordination number of 4? What is the most common structure observed for coordination number 6?

22.13 Sketch the structure of an octahedral complex that contains only identical monodentate ligands. Use *M* for the metal and *L* for the ligand.

22.14 Sketch the structure of the octahedral $[\mathrm{Co(EDTA)}]^-$ ion. Remember that adjacent donor atoms in a polydentate ligand span adjacent positions in the octahedron.

Isomers of Coordination Compounds

22.15 What are *isomers*?

22.16 Define *stereoisomerism*, *geometric isomerism*, *chiral isomers*, and *enantiomers*.

22.17 What are *cis* and *trans isomers*?

22.18 What condition must be fulfilled in order for a molecule or ion to be chiral?

22.19 What are optical isomers?

22.20 What are the differences between optical and geometric isomers?

Bonding in Complexes

22.21 On appropriate coordinate axes, sketch and label the five *d* orbitals.

22.22 Which *d* orbitals point *between* the *x*, *y*, and *z* axes? Which point *along* the coordinate axes?

22.23 Explain why an electron in a $d_{x^2-y^2}$ or d_{z^2} orbital in an octahedral complex will experience greater repulsions because of the presence of the ligands than an electron in a d_{xy}, d_{xz}, or d_{yz} orbital.

22.24 Sketch the *d*-orbital energy level diagram for a typical octahedral complex.

22.25 Explain why octahedral cobalt(II) complexes are easily oxidized to cobalt(III) complexes. Sketch the *d*-orbital energy diagram and assume a large value of Δ when placing electrons in the *d* orbitals.

22.26 Explain how the same metal in the same oxidation state is able to form complexes of different colors.

22.27 If a complex appears red, what color light does it absorb? What color light is absorbed if the complex appears yellow?

22.28 What does the term *spectrochemical series* mean? How can the order of the ligands in the series be determined?

22.29 What do the terms *low-spin complex* and *high-spin complex* mean?

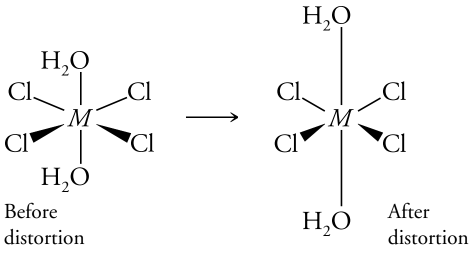
22.30 For which *d*-orbital electron configurations are both high-spin and low-spin octahedral complexes possible?

22.31 What factors about the metal and ligands affect the magnitude of Δ?

22.32 Indicate by means of a sketch what happens to the *d*-orbital electron configuration of the $[Fe(CN)_6]^{4-}$ ion when it absorbs a photon of visible light.

22.33 The complex $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. Sketch the *d*-orbital energy level diagram for this complex and indicate the electron populations of the orbitals.

22.34 Consider the complex $[M(H_2O)_2Cl_4]^-$ illustrated below on the left. Suppose the structure of this complex is distorted to give the structure on the right, where the water molecules along the *z* axis have moved away from the metal somewhat and the four chloride ions along the *x* and *y* axes have moved closer. What effect will this distortion have on the energy level splitting pattern of the *d* orbitals? Use a sketch of the splitting pattern to illustrate your answer.



Biological Functions of Metals Ions

22.35 In what ways is the porphyrin structure important in biological systems?

22.36 If a metal ion is held in the center of a porphyrin ring structure, what is its coordination number? (Assume the porphyrin is the only ligand.)

22.37 What function does heme serve in hemoglobin? What does it do in myoglobin?

22.38 How are the ligand ring structures similar in vitamin B_{12} and in heme? What metal is coordinated in cobalamin?

22.39 What are some of the roles played by calcium ion in the body?

Review Problems

Complex Ions

22.40 The iron(III) ion forms a complex with six cyanide ions that is often called the ferricyanide ion. What is the net charge on this complex ion, and what is its formula? What is the IUPAC name for the complex?

22.41 The silver ion forms a complex ion with two ammonia molecules. What is the formula of this ion, and what is its IUPAC name? Can this complex ion exist as a salt with the sodium ion or with the chloride ion? Write the formula of the possible salt. (Use brackets and parentheses correctly.)

22.42 Write the formula, including its correct charge, for a complex that contains Co^{3+}, two Cl^-, and two ethylenediamine ligands.

OH **22.43** Write the formula, including its correct charge, for a complex that contains Cr^{3+}, two NH_3 ligands, and four NO_2^- ligands.

Metal Complex Nomenclature

22.44 How would the following molecules or ions be named as ligands when writing the name of a complex ion?

(a) $C_2O_4^{2-}$ **(b)** S^{2-} **(c)** Cl^-
(d) $(CH_3)_2NH$ (dimethylamine)

OH **22.45** How would the following molecules or ions be named as ligands when writing the name of a complex ion?

(a) NH_3 **(b)** N^{3-} **(c)** SO_4^{2-} **(d)** $C_2H_3O_2^-$

22.46 Give IUPAC names for each of the following:

(a) $[Ni(NH_3)_6]Cl_2$

(b) $[CrCl_3(NH_3)_3]^-$

(c) $[Co(NO_2)_6]^{3-}$

(d) $[Mn(CN)_4(NH_3)_2]^{2-}$

(e) $K_3[Fe(C_2O_4)_3]$

22.47 Give IUPAC names for each of the following:
- **(a)** $[AgI_2]^-$
- **(b)** $[SnS_3]^{2-}$
- **(c)** $[Co(en)_2(H_2O)_4]_2(SO_4)_3$
- **(d)** $[CrCl(NH_3)_5]SO_4$
- **(e)** $K_3[Co(C_2O_4)_3]$

22.48 Write chemical formulas for each of the following:
- **(a)** tetraaquadicyanoiron(III) ion
- **(b)** tetraammineoxalatonickel(II)
- **(c)** pentaaquahydroxoaluminum(III) chloride
- **(d)** potassium hexathiocyanatomanganate(III)
- **(e)** tetrachlorocuprate(II) ion

22.49 Write chemical formulas for each of the following:
- **(a)** tetrachloroaurate(III) ion
- **(b)** bis(ethylenediamine)dinitroiron(III) ion
- **(c)** tetraamminedicarbonatocobalt(III) nitrate
- **(d)** ethylenediaminetetraacetatoferrate(II) ion
- **(e)** diamminedichloroplatinum(II)

Coordination Number and Structure

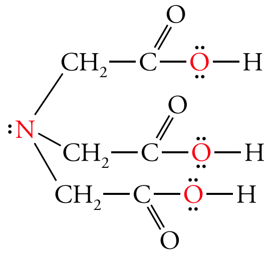
22.50 What is the coordination number of Fe in $[FeCl_2(H_2O)_2(en)]$? What is the oxidation number of iron in this complex?

OH **22.51** What is the coordination number of nickel in $[Ni(C_2O_4)_2(NO_2)_2]^{4-}$?

22.52 Draw a reasonable structure for **(a)** $[Zn(NH_3)_4]^{2+}$ and **(b)** trioxalatochromate(III) ion.

22.53 Draw a reasonable structure for **(a)** $[CoBr(NH_3)_3]^{2+}$ and **(b)** dichloroethylenediamineplatinum(II).

22.54 NTA is the abbreviation for nitrilotriacetic acid, a substance that was used at one time in detergents. Its structure is



The four donor atoms of this ligand are shown in red. Sketch the structure of an octahedral complex containing this ligand. Assume that two water molecules are also attached to the metal ion and that each oxygen donor atom in the NTA is bonded to a position in the octahedron that is adjacent to the nitrogen of the NTA.

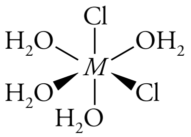
22.55 The following compound is called diethylenetriamine and is abbreviated "dien":

$$H_2\ddot{N}{-}CH_2{-}CH_2{-}\ddot{N}H{-}CH_2{-}CH_2{-}\ddot{N}H_2$$

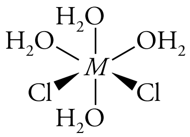
When it bonds to a metal, it is a ligand with three donor atoms.
- **(a)** Which are most likely the donor atoms?
- **(b)** What is the coordination number of cobalt in the complex $Co(dien)_2{}^{3+}$?
- **(c)** Sketch the structure of the complex $[Co(dien)_2]^{3+}$.
- **(d)** Which complex would be expected to be more stable in aqueous solution, $[Co(dien)_2]^{3+}$ or $[Co(NH_3)_6]^{3+}$?
- **(e)** What would be the structure of triethylenetetraamine?

Isomers of Metal Complexes

22.56 Below are two structures drawn for a complex. Are they actually different isomers, or are they identical? Explain your answer.

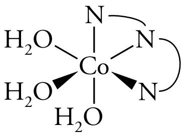


Structure I



Structure II

***22.57** Below is a structure for one of the isomers of the complex $[Co(H_2O)_3(dien)]^{3+}$. Are isomers of this complex chiral? Justify your answer. See Problem 22.55.



N⌒N⌒N represents dien

22.58 Sketch and label the isomers of the square planar complex $[PtBrCl(NH_3)_2]$.

22.59 The complex $[CoCl_3(NH_3)_3]$ can exist in two isomeric forms. Sketch them.

22.60 Sketch the chiral isomers of $[Co(C_2O_4)_3]^{3-}$.

OH **22.61** Sketch the chiral isomers of $[CrCl_2(en)_2]^+$. Is there a nonchiral isomer of this complex?

Bonding in Metal Complexes

22.62 In which complex do we expect to find the larger Δ?
- **(a)** $[Cr(H_2O)_6]^{2+}$ or $[Cr(H_2O)_6]^{3+}$
- **(b)** $[Cr(en)_3]^{3+}$ or $[CrCl_6]^{3-}$

22.63 Arrange the following complexes in order of increasing wavelength of the light absorbed by them: $[Cr(H_2O)_6]^{3+}$, $[CrCl_6]^{3-}$, $[Cr(en)_3]^{3+}$, $[Cr(CN)_6]^{3-}$, $[Cr(NO_2)_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$.

OH **22.64** Which complex should be expected to absorb light of the highest frequency, $[Cr(H_2O)_6]^{3+}$, $[Cr(en)_3]^{3+}$, or $[Cr(CN)_6]^{3-}$?

22.65 Which complex should absorb light at the longer wavelength?

(a) $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$

(b) $[Mn(CN)_6]^{3-}$ or $[Mn(CN)_6]^{4-}$

22.66 In each pair below, which complex is expected to absorb light of the shorter wavelength? Justify your answers.

(a) $[RuCl(NH_3)_5]^{2+}$ or $[FeCl(NH_3)_5]^{2+}$

(b) $[Ru(NH_3)_6]^{2+}$ or $[Ru(NH_3)_6]^{3+}$

22.67 A complex $[CoA_6]^{3+}$ is red. The complex $[CoB_6]^{3+}$ is green. Which ligand, A or B, produces the larger crystal field splitting, Δ? Explain your answer.

22.68 Referring to the two ligands, A and B, described in Problem 22.67, which complex would be expected to be more easily oxidized, $[CoA_6]^{2+}$ or $[CoB_6]^{2+}$? Explain your answer.

22.69 Referring to the complexes in Problems 22.67 and 22.68, would the color of $[CoA_6]^{2+}$ more likely be red or blue?

22.70 Would the complex $[CoF_6]^{4-}$ more likely be low-spin or high-spin? Could it be diamagnetic?

22.71 Sketch the *d*-orbital energy level diagrams for $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ and predict the number of unpaired electrons in each.

Additional Exercises

22.72 Ni^{2+} ions can be either four coordinate or six coordinate; which one is more likely to be a red compound and which is likely to be a blue compound?

22.73 For the complex $(NH_4)_2[Pd(SCN)_4]$, draw the structure of the free ligand, draw the structure of the complex, indicate the shape of the complex, and give the oxidation state of the central metal ion.

22.74 Most of the first row transition metals form 2+ ions, while other oxidation states are less common. Why do these metals form 2+ ions?

22.75 Is the complex $[Co(EDTA)]^-$ chiral? Illustrate your answer with sketches.

22.76 The complex $[PtCl_2(NH_3)_2]$ can be obtained as two distinct isomeric forms. Make a model of a tetrahedron and show that if the complex were tetrahedral, two isomers would be impossible.

22.77 $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$ are both linear complexes. Draw the crystal field energy level diagram for the *d*-orbitals for a linear complex, if the ligands lie along the *z* axis.

OH ***22.78** A solution was prepared by dissolving 0.500 g of $CrCl_3 \cdot 6H_2O$ in 100 mL of water. A silver nitrate solution was added and gave a precipitate of AgCl that was filtered from the mixture, washed, dried, and weighed. The AgCl had a mass of 0.538 g.

(a) What is the formula of the complex ion of chromium in this compound?

(b) What is the correct formula for the compound?

(c) Sketch the structure of the complex ion in this compound.

(d) How many different isomers of the complex can be drawn?

***22.79** The compound $Cr_2(NH_3)_3(H_2O)_3Cl_6$ is a neutral salt in which the cation and anion are both octahedral complex ions. How many isomers (including possible structural and chiral isomers) are there that have this overall composition?

***22.80** The complex $[Co(CN)_6]^{4-}$ is not expected to be perfectly octahedral. Instead, the ligands in the *xy* plane are pulled closer to the Co^{2+} ion while those along the *z* axis move slightly farther away. Using information available in this chapter, explain why the distortion of the octahedral geometry leads to a net lowering of the energy of this complex.

22.81 Sketch all of the isomers of $[CoCl_2(en)(NH_3)_2]^+$. Label the *cis* chloro and *trans* chloro isomers.

22.82 Copper(II) aqueous solutions are blue and zinc(II) aqueous solutions are colorless. Why?

Multi-Concept Problems

22.83 Silver plating processes often use $Ag(CN)_2^-$ as the source for Ag^+ in solution. To make the solution, a chemist used 4.0 L of 3.00 *M* NaCN and 50 L of 0.2 *M* $AgNO_3$. What is the concentration of free Ag^+ ions? Why is AgCl not used in this process?

***22.84** Cobalt forms complexes in both the +2 and +3 oxidation states. The standard reduction potential for Co^{3+} to Co^{2+} is 1.82 V. In water, the species in solution is $[Co(H_2O)_6]^{3+}$. The equilibrium constants for the formation of the hexaammine complexes are as follows:

$$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad K_{form} = 1.3 \times 10^{14}$$

$$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+} \qquad K_{form} = 4.8 \times 10^{48}$$

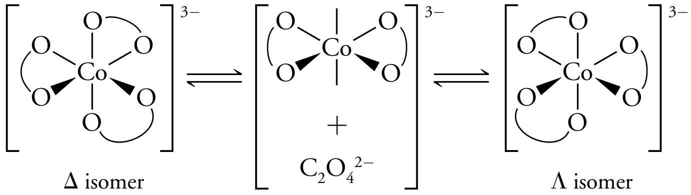
Why is the cobalt(III) complex more stable than the cobalt(II) species? What is the reduction potential for the reduction of $[Co(NH_3)_6]^{3+}$? Which is a stronger oxidizing agent, $[Co(NH_3)_6]^{3+}$ or $[Co(H_2O)_6]^{3+}$?

***22.85** Platinum(IV) makes compounds with coordination numbers of 6. A Pt^{4+} compound was made with chloride and amine ligands. The empirical formula for the compound was determined to be $PtCl_4(NH_3)_6$. The isolated compound has an osmotic pressure of 0.734 atm for a 0.1 *M* solution, and when 0.126 g of the compound was reacted with $AgNO_3$, 0.0209 g of AgCl was formed. How many ions does the compound form in water? What is the structure of this compound? What other isomers could have been formed? How many ions would they have released in solution?

Exercises in Critical Thinking

22.86 It was mentioned in footnote 5 on page 456 that *d* orbitals are capable of participating in the formation of π bonds. Make a sketch that illustrates how such a bond could be formed between two *d* orbitals and between a *d* and a *p* orbital.

22.87 The two chiral isomers of $[Co(C_2O_4)_3]^{3-}$ (shown at the right) can be viewed as propellers having either a right- or left-handed twist, respectively. They are identified by the labels Δ and Λ, as indicated. A 50–50 mixture of both isomers is said to be *racemic* and will not rotate plane polarized light. Using various laboratory procedures, the two isomers present in a racemic mixture can be separated from each other. For this complex, however, a solution of a single isomer is unstable and gradually reverts to a mixture of the two isomers by a process called *racemization*. Racemization involves the conversion of one isomer to the other until an equilibrium between the two isomers is achieved (i.e., $\Delta \rightleftharpoons \Lambda$). One mechanism proposed for the racemization of the isomers of $[Co(C_2O_4)_3]^{3-}$ involves the dissociation of an oxalate ion followed by the rearrangement and then the reattachment of $C_2O_4^{2-}$.



What experiment could you perform to test whether this is really the mechanism responsible for the racemization of $[Co(C_2O_4)_3]^{3-}$?

23 Organic Compounds, Polymers, and Biochemicals

Chapter Outline

23.1 | The Nature of Organic Chemistry

23.2 | Hydrocarbons

23.3 | Organic Compounds Containing Oxygen

23.4 | Organic Derivatives of Ammonia

23.5 | Organic Polymers

23.6 | Biochemical Compounds

23.7 | Nucleic Acids

It's difficult to find anyone who has not watched at least one of the CSI crime shows. Crime scene investigators gather evidence of various kinds, including samples of human tissue and bodily fluids. As is well known now, such samples can be subjected to DNA analysis, and a match between a crime scene sample and a suspect is very convincing evidence that the suspect was involved in some way with the crime. This is because a person's DNA differs from that of all other individuals on earth (except if the person has an identical twin). DNA is what makes us unique and is one of the biochemical compounds discussed in this chapter. Robert Prezioso/Getty Images, Inc.

This Chapter in Context

In Section 9.6 we noted that many of the substances we encounter on a daily basis have molecular structures based on atoms of carbon linked to one another by covalent bonds. You've already seen a variety of them as examples used in discussions throughout this book. They include such substances as hydrocarbons, alcohols, ketones (such as acetone), and organic acids. The number of such compounds is enormous and their study constitutes the branch of chemistry called *organic chemistry*, so named because at one time it was believed that such substances could only be synthesized by living organisms.

At the molecular level of life, nature uses compounds of carbon. The amazing variety of living systems, down to the uniqueness of each individual, is possible largely because of the properties of this element. We'll take a look at some biologically important kinds of carbon compounds near the end of this chapter.

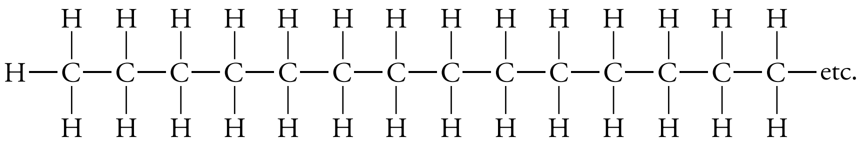
23.1 | The Nature of Organic Chemistry

Organic chemistry is the study of the preparation, properties, and reactions of those compounds of carbon not classified as inorganic. The latter include the oxides of carbon, the bicarbonates and carbonates of metal ions, the metal cyanides, and a handful of other compounds. There are tens of millions of known carbon compounds, and all but a very few are classified as organic.

Uniqueness of the Element Carbon

■ Sulfur atoms can also form long chains, but they are unable to bond to the atoms of any other element strongly at the same time.

What makes the existence of so many organic compounds possible is the ability of carbon atoms to form strong covalent bonds to each other *while at the same time bonding strongly to atoms of other nonmetals*. For example, molecules in the plastic polyethylene have *carbon chains* that are thousands of carbon atoms long, with hydrogen atoms attached to each carbon.



$$\begin{array}{ccccccccccccccc}
 & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & | \\
\mathrm{H}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}-\text{etc.} \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & | \\
 & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H}
\end{array}$$

polyethylene (small segment of one molecule)

The longest known sequence of atoms of the other members of Group 4A, each also bonded to hydrogen atoms, is eight for silicon, five for germanium, two for tin, and one for lead.

■ The isomers of butane were also discussed on page 373.

Another reason for the huge number of organic compounds is *isomerism*, which was mentioned briefly in Chapter 9 on page 374. (Isomerism among complex ions is discussed in Chapter 22.) Recall that *isomers* are compounds with identical molecular formulas, but whose molecules have different structures. There are a number of different kinds of isomers, as we will discuss below. Two examples of isomers of C_4H_{10} and of C_2H_6O are shown in Figure 23.1. Notice the tetrahedral arrangement of atoms around each of the carbon atoms. This tetrahedral geometry is found whenever carbon is bonded to other atoms by just single bonds.

The structural formulas of the compounds in Figure 23.1 can be represented in different ways. Complete Lewis structures can be drawn showing all of the bonds between atoms.

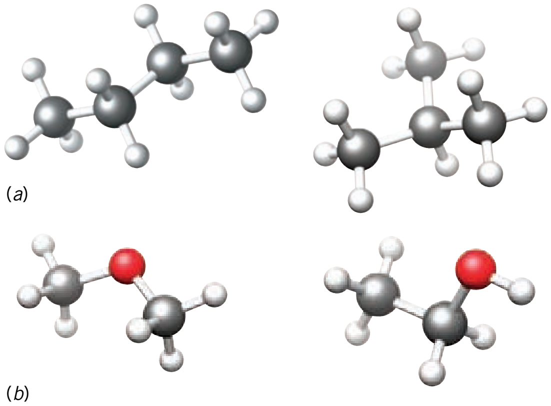
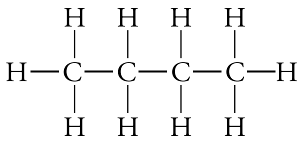
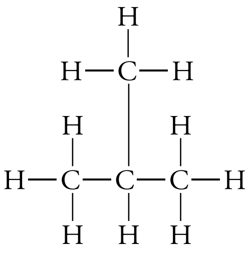
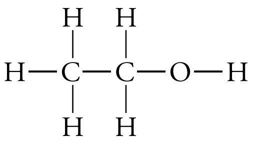
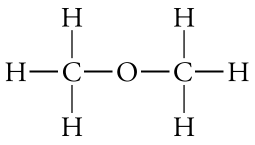


Figure 23.1 | **Isomers.** (*a*) The isomers of C_4H_{10}. Butane is on the left and methylpropane (isobutane) is on the right. (*b*) The isomers of C_2H_6O. Dimethyl ether is on the left and ethanol is on the right.


butane
BP −0.5 °C


2-methylpropane
(isobutane)
BP −11.7 °C


ethanol
BP 78.5 °C


dimethyl ether
BP −23 °C

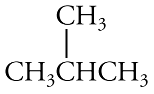
Notice that each isomer has a different boiling point. As we noted in Chapter 9, isomers are different chemical substances, each with its own set of properties.

■ VSEPR theory permits us to predict the tetrahedral geometry around carbon observed in Figure 23.1.

To save space and time when writing structural formulas we can write **condensed structural formulas** (also called **condensed structures**) such as those below, in which the C—H, C—C, and C—O bonds are "understood." We can do this because in nearly all organic compounds carbon forms four bonds, nitrogen forms three, oxygen forms two, and hydrogen forms one.

Condensed structures

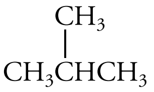
$CH_3CH_2CH_2CH_3$
butane


$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CHCH_3}}$$
methylpropane
(isobutane)

CH_3CH_2OH
ethanol

CH_3OCH_3
dimethyl ether

Take a moment to compare the condensed structural formulas with the full Lewis structures. Also note that there can be more than one way to write a condensed structure, as illustrated by 2-methylpropane.


$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CHCH_3}} \quad \text{or} \quad CH_3CH(CH_3)CH_3 \quad \text{or} \quad (CH_3)_3CH$$

We will use condensed structures frequently throughout this chapter. *In writing condensed structures, be sure there are sufficient numbers of hydrogens so that the total number of bonds to each carbon equals four.*

In Chapter 22 we described the chiral properties of certain isomers. An organic compound exhibits chirality when it contains an **asymmetric carbon atom,** which is a carbon atom that is bonded to four different atoms or groups. An example is butan-2-ol (also called

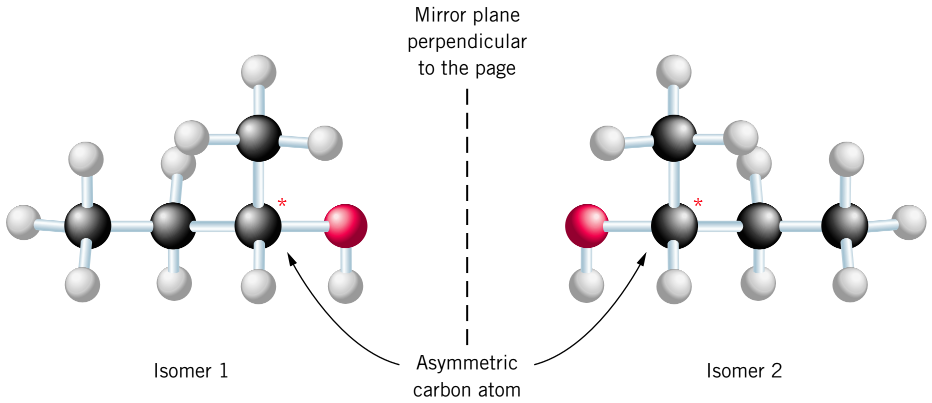
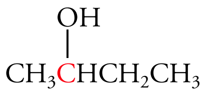


Figure 23.2 | **Chiral isomers of butan-2-ol.** Isomer 2 is the mirror image of Isomer 1. No matter how you twist or turn Isomer 1, you cannot get it to fit exactly onto Isomer 2, which means the two isomers are nonsuperimposable mirror images of each other.

2-butanol) in which the asymmetric carbon atom, marked with a red asterisk, is bonded to H, OH, CH_3, and CH_2CH_3.



$$\mathrm{CH_3}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH_3}$$

butan-2-ol
2-butanol

The two nonsuperimposable mirror image isomers of this compound, also called optical isomers or stereoisomers, are shown in Figure 23.2.

The table in the margin illustrates that as the number of carbons per molecule increases, the number of possible isomers for any given formula becomes enormous.

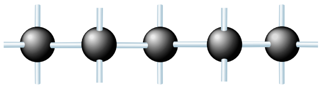
■ Few of the possible isomers of the compounds with large numbers of carbon atoms have actually been made, but there is nothing except too much crowding within the molecules of some of them to prevent their existence.

Formula	**Number of Isomers**
C_8H_{18}	18
$C_{10}H_{22}$	75
$C_{20}H_{42}$	366,319
$C_{40}H_{82}$	6.25×10^{13} (estimated)

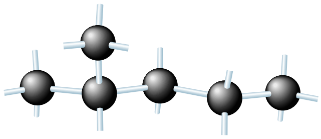
Open-Chain and Ring Compounds

The continuous sequence of carbon atoms in polyethylene (page 1048) is called a **straight chain**. This means *only* that no carbon atom bonds to more than two other carbons. It does not refer to the *shape* of the molecule. If we made a molecular model of polyethylene and coiled it into a spiral, we would still say that its carbon skeleton has a straight chain. It has no branches.

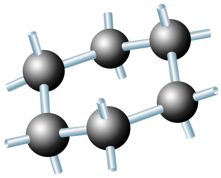
Branched chains are also very common. For example, isooctane, the standard for the octane rating of gasoline, has a *main chain* of five carbon atoms (in black) carrying three CH_3 *branches* (shown in red).



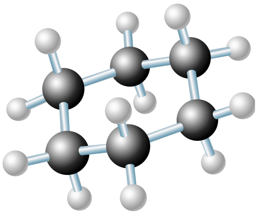
Straight chain



Branched chain

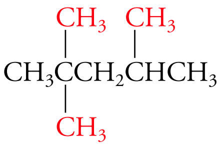


Carbon ring



Cyclohexane

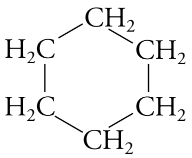
■ Isooctane, one of the many alkanes in gasoline, is the standard for the octane ratings of various types of gasoline. Pure isooctane is assigned an octane rating of 100.



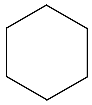
$$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_3}$$

isooctane

Carbon rings are also common. Cyclohexane, for example, has a ring of six carbon atoms:



cyclohexane



cyclohexane
(fully condensed)

Just about everything is "understood" in the very convenient, fully condensed structure of cyclohexane. When polygons, like the hexagon, are used to represent rings, the following conventions are used:

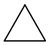
Using Polygons to Represent Rings

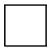
1. C occurs at each corner unless O or N (or another atom capable of forming more than one bond) is explicitly written at a corner.
2. A line connecting two corners is a covalent bond (single bond) between adjacent ring atoms.
3. Remaining bonds, as required by the carbon at a corner to have a total of four bonds, are understood to hold H atoms.
4. Double bonds are always explicitly shown.

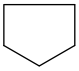
TOOLS

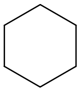
Polygons as condensed structures

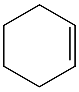
We can illustrate these rules with the following cyclic compounds:

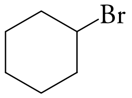

cyclopropane


cyclobutane


cyclopentane


cyclohexane

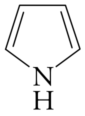

cyclohexene



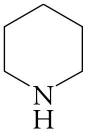
bromocyclohexane

There is no theoretical upper limit to the size of a ring.

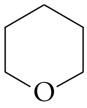
Many compounds have **heterocyclic** rings. Their molecules carry an atom other than carbon in a ring position, as in pyrrole, piperidine, and tetrahydropyran.



pyrrole



piperidine



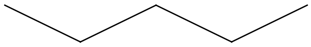
tetrahydropyran

The tetrahydropyran ring occurs in molecules of sugar.

The atom other than carbon is called the *heteroatom*, and any atoms of H or other element bonded to it are not "understood" but are always shown.

Notation similar to that for rings is often used for open-chain molecules as well. For example, the structure of pentane can be represented as follows:

$$H_3C-CH_2-CH_2-CH_2-CH_3$$



pentane

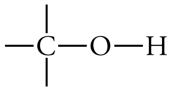
On the right, the four bonds between carbon atoms are represented by four connected line segments. At the end of each line segment (including where line segments join) there is a carbon atom plus enough hydrogen atoms to account for the four bonds that the carbon must have.

Organic Families and Their Functional Groups

The study of the huge number of organic compounds is manageable because they can be sorted into *organic families* defined by *functional groups*, a number of which were described in Chapter 9 and summarized in Table 9.2 on page 375. A more complete list is found in Table 23.1. In the pages ahead we will examine some of the reactions of functional groups.

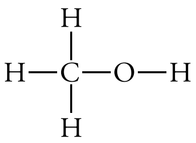
Functional groups are small structural units within molecules at which most of the compound's chemical reactions occur. For example, all *alcohols* have the *alcohol group,* which imparts certain chemical properties that are common to them all. The simplest member of the alcohol family, methanol (also called methyl alcohol), has molecules with only one carbon. Ethanol molecules have two carbons. Similarly, all members of the family of *carboxylic acids* (organic acids) have the *carboxyl group.* The carboxylic acid with two carbons per molecule is the familiar weak acid, ethanoic acid (better known as acetic acid).

Recall from Chapter 9 that organic acids contain the carboxyl group.



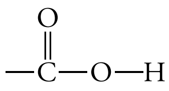
$$-\overset{|}{\underset{|}{C}}-O-H$$

alcohol group



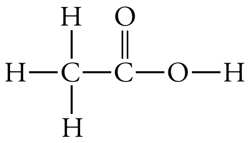
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H$$

methanol
(methyl alcohol)



$$-\overset{\overset{O}{\|}}{C}-O-H$$

carboxyl group

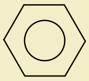
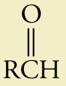
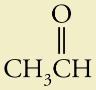
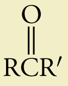
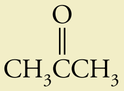
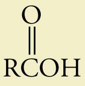
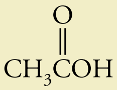
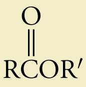
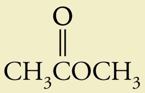
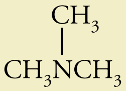
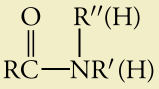
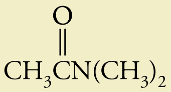


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H$$

ethanoic acid
(acetic acid)

Functional groups

Table 23.1 Some Important Families of Organic Compounds

Family	Characteristic Structural Feature[a]	Example
Hydrocarbons	Only C and H present	
	Families of Hydrocarbons:	
	Alkanes: only single bonds	CH_3CH_3
	Alkenes: $C{=}C$	$CH_2{=}CH_2$
	Alkynes: $C{\equiv}C$	$HC{\equiv}CH$
	Aromatic: Benzene ring	
Alcohols	ROH	CH_3CH_2OH
Ethers	ROR′	CH_3OCH_3
Aldehydes	 $R\overset{O}{\overset{\|}{C}}H$	 $CH_3\overset{O}{\overset{\|}{C}}H$
Ketones	 $R\overset{O}{\overset{\|}{C}}R'$	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$
Carboxylic acids	 $R\overset{O}{\overset{\|}{C}}OH$	 $CH_3\overset{O}{\overset{\|}{C}}OH$
Esters	 $R\overset{O}{\overset{\|}{C}}OR'$	 $CH_3\overset{O}{\overset{\|}{C}}OCH_3$
Amines	RNH_2, RNHR′, RNR′R″	CH_3NH_2 CH_3NHCH_3  $CH_3\overset{CH_3}{\overset{|}{N}}CH_3$
Amides	 $R\overset{O}{\overset{\|}{C}}-\overset{R''(H)}{\overset{|}{N}}R'(H)$	 $CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2$

[a] R, R′, and R″ represent hydrocarbon groups—*alkyl groups*—defined in the text.

One family in Table 23.1, the *alkane* family, has no functional group, just C—C and C—H single bonds. These bonds are virtually nonpolar, because C and H are so alike in electronegativity. Therefore, alkane molecules are the least able of all organic molecules to attract ions or polar molecules. As a result, they do not react, at least at room temperature, with polar or ionic reactants such as strong acids and bases and common oxidizing agents, like dichromate or permanganate ions.

The Symbol R in Structural Formulas

In Tables 9.2 and 23.1 the functional groups are shown attached to the symbol R. Chemists use the symbol R in a structure to represent purely alkane-like hydrocarbon groups, which are unreactive toward substances that are able to react with the functional group. For example, one type of amine is represented by the formula $R—NH_2$, where R could be CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and so forth. Because the amines are compounds with an ammonia-like group, they are weak Brønsted bases and, like ammonia, react with hydronium ions. We can, therefore, summarize in just one equation the reaction of a strong acid with *any* amine of the R—NH_2 type, regardless of how large the hydrocarbon portion of the molecule is, by the following equation:

$$R{-}NH_2 + H_3O^+ \longrightarrow R{-}NH_3^+ + H_2O$$

23.2 | Hydrocarbons

Petroleum refinery. The towers contain catalysts that break up large molecules in hot crude oil to smaller molecules suitable for vehicle engines. *(Martin Bond/ Photo Researchers)*

Hydrocarbons are compounds whose molecules consist of only C and H atoms. The *fossil fuels*—coal, petroleum, and natural gas—supply us with virtually all of these substances. One of the operations in petroleum refining is to boil crude oil (petroleum from which natural gas has been removed) and selectively condense the vapors between preselected temperature ranges. *Gasoline*, for example, is the fraction boiling roughly between 40 and 200 °C and is composed of molecules that have 5 to 12 carbon atoms. The *kerosene* and *jet fuel* fraction contains molecules with more carbon atoms and overlaps this range, going from 175 to 325 °C.

Hydrocarbons can be divided into four types: *alkanes*, *alkenes*, *alkynes*, and *aromatic hydrocarbons* (Table 23.1). All are insoluble in water. All burn, giving carbon dioxide and water if sufficient oxygen is available.

■ Recall from Section 6.5 that in insufficient oxygen, some carbon monoxide and carbon also form when hydrocarbons burn.

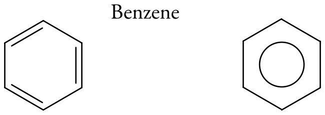
The **alkanes**, mentioned earlier, contain carbon atoms bonded to other atoms by only single bonds. In the alkanes all of the carbon atoms use sp^3 hybrid orbitals for bonding, so the orientation of atoms around each carbon is tetrahedral. Open-chain members of the alkane family have the general formula C_nH_{2n+2}.

Alkenes contain one or more carbon–carbon double bonds of the type described in Figure 10.32 on page 441. **Alkynes** contain one or more triple bonds formed as shown in Figure 10.35 on page 444. Alkenes and alkynes are said to be **unsaturated compounds** because under appropriate conditions their molecules can take up additional H atoms to give alkane molecules. We will study these reactions later. The alkanes are **saturated compounds**, compounds with only single bonds, and do not take on additional H atoms.

■ Alkanes are saturated in the sense that they have as many hydrogen atoms as the carbon atoms can hold, just as a saturated solution has as much solute as it can hold.

The **aromatic hydrocarbons**, typified by benzene, are also unsaturated because the carbon atoms of their rings, when represented by simple Lewis structures, also have double bonds.

Benzene



Lewis structure (one of two resonance structures)

Alternative structure that emphasizes delocalized bonding

The delocalized nature of the π bond system in the ring causes them to behave quite differently from alkenes and alkynes in their chemical reactions, as we discuss later.

IUPAC Nomenclature of Alkanes

The **IUPAC rules** for naming organic compounds follow a regular pattern. The last syllable in an IUPAC name designates the family of the compound. The names of all saturated hydrocarbons, for example, end in *-ane*. For each family there is a rule for picking out and naming the *parent chain* or *parent ring* within a specific molecule. The compound is then regarded as having *substituents* attached to its parent chain or ring. Let's see how these principles work with naming alkanes.

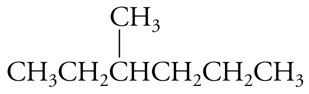
■ In earlier discussions we gave both the official IUPAC names as well as common names for organic compounds.

Naming alkanes

IUPAC Rules for Naming the Alkanes

1. The name ending for all alkanes (and cycloalkanes) is *-ane*.

2. The *parent chain* is the longest continuous chain of carbons in the structure. For example, the branched-chain alkane

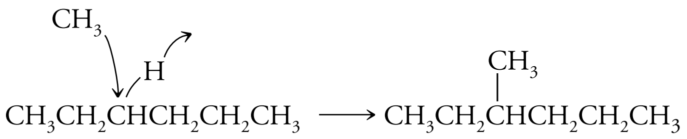


$$\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3}$$

is regarded as being "made" from the following parent

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_3}$$

by replacing a hydrogen atom on the third carbon from the left with CH_3.



$$\mathrm{CH_3CH_2\overset{CH_3\quad H}{C}HCH_2CH_2CH_3 \longrightarrow CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3}$$

3. A prefix is attached to the name ending, *-ane,* to specify the number of carbon atoms *in the parent chain*. The prefixes through chain lengths of 10 carbons are as follows. The names in Table 23.2 show their use.

meth-	1 C	hex-	6 C
eth-	2 C	hept-	7 C
prop-	3 C	oct-	8 C
but-	4 C	non-	9 C
pent-	5 C	dec-	10 C

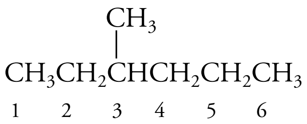
The parent chain of our example has six carbons, so the parent is named hexane—*hex* for six carbons and *ane* for being in the alkane family. Therefore, the alkane whose name we are devising is viewed as a *derivative* of this parent, *hexane*.

4. The carbon atoms of the parent chain are numbered starting from whichever end of the chain gives the location of the first branch the lower of two possible numbers. Thus, the correct direction for numbering our example is from left to

Table 23.2 Straight-Chain Alkanes

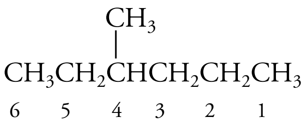
IUPAC Name	Molecular Formula	Structure	Boiling Point (°C)	Melting Point (°C)	Density (g mL^{-1}, 20 °C)
Methane	CH_4	CH_4	−161.5	−182.5	
Ethane	C_2H_6	CH_3CH_3	−88.6	−183.3	
Propane	C_3H_8	$CH_3CH_2CH_3$	−42.1	−189.7	
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	−0.5	−138.4	
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36.1	−129.7	0.626
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.659
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.684
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	125.7	−56.8	0.703
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.718
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174.1	−29.7	0.730

right, not right to left, because this locates the branch (CH_3) at position 3, not position 4.



$$\overset{\displaystyle CH_3}{}\;CH_3CH_2\underset{}{C}HCH_2CH_2CH_3$$

(correct direction of numbering)



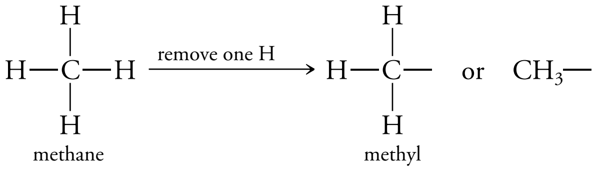
$$CH_3CH_2\overset{\displaystyle CH_3 \atop |}{C}HCH_2CH_2CH_3$$

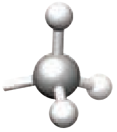
(incorrect direction of numbering)

5. Each branch attached to the parent chain is named, so we must now learn the names of some of the alkane-like branches.

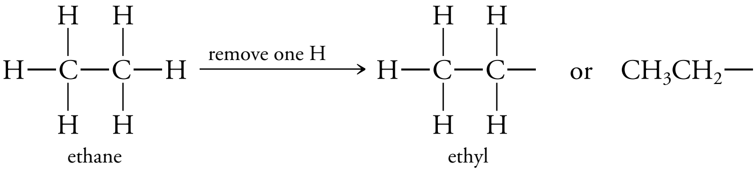
Alkyl Groups

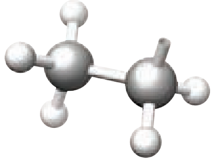
Any branch that consists only of carbon and hydrogen and has only single bonds is called an **alkyl group,** and the names of all alkyl groups end in *-yl.* Think of an alkyl group as an alkane minus one of its hydrogen atoms. For example,


remove one H
methane
methyl
or CH_3—



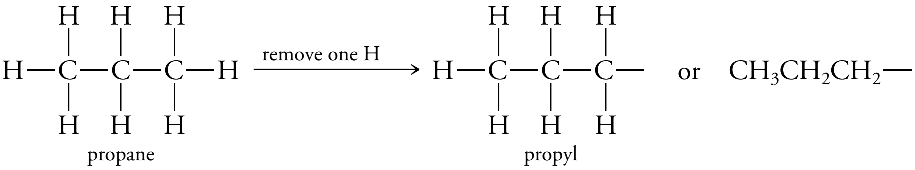
methyl group

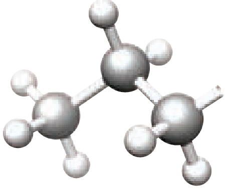

remove one H
ethane
ethyl
or CH_3CH_2—



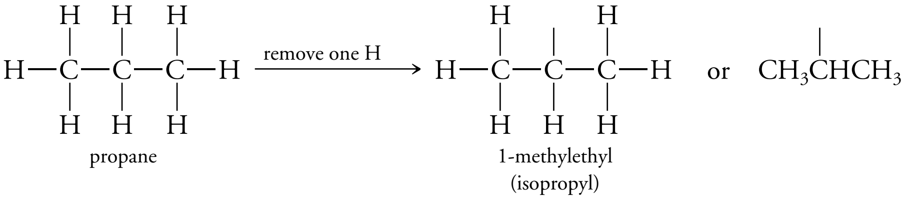
ethyl group

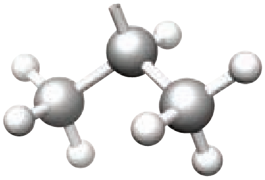
Two alkyl groups can be obtained from propane because the middle position in its chain of three is not equivalent to either of the end positions.


remove one H
propane
propyl
or $CH_3CH_2CH_2$—



propyl group


remove one H
propane
1-methylethyl
(isopropyl)
or CH_3CHCH_3

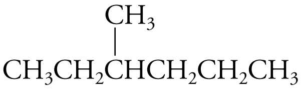


1-methylethyl group
(isopropyl group)

■ Isopropyl is the common name; 1-methylethyl is the official IUPAC name.

We will not need to know the IUPAC names for any alkyl groups with four or more carbon atoms. Now let's continue with our IUPAC rules.

6. The name of each alkyl group is attached to the name of the parent as a prefix, placing its chain location number in front, separating the number from the name by a hyphen. Thus, the original example is named 3-methylhexane.

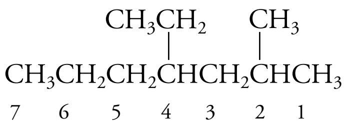


$$CH_3CH_2\overset{\displaystyle CH_3 \atop |}{C}HCH_2CH_2CH_3$$

3-methylhexane

7. When two or more groups are attached to the parent, each is named and located with a number. The names of alkyl substituents are assembled in their alphabetical

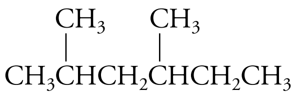
order. Always use *hyphens* to separate numbers from words. The following molecule provides an illustration:



$$\begin{array}{c} \mathrm{CH_3CH_2}\quad\ \mathrm{CH_3} \\ \mathrm{CH_3CH_2CH_2\overset{|}{C}HCH_2\overset{|}{C}HCH_3} \\ 7\quad 6\quad 5\quad 4\quad 3\quad 2\quad 1 \end{array}$$

4-ethyl-2-methylheptane

8. When two or more substituents are identical, multiplier prefixes are used: di- (for 2), tri- (for 3), tetra- (for 4), and so forth. The location number of every group must occur in the final name. Always separate a number from another number in a name by a *comma*. For example,

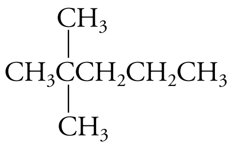


$$\begin{array}{c} \mathrm{CH_3}\quad\ \mathrm{CH_3} \\ \mathrm{CH_3\overset{|}{C}HCH_2\overset{|}{C}HCH_2CH_3} \end{array}$$

Correct name: 2,4-dimethylhexane

Incorrect names: 2,4-methylhexane
3,5-dimethylhexane
2-methyl-4-methylhexane
2-4-dimethylhexane

9. When identical groups are on the *same* carbon, the number of this position is repeated in the name. For example,



$$\begin{array}{c} \mathrm{CH_3} \\ \mathrm{CH_3\overset{|}{\underset{|}{C}}CH_2CH_2CH_3} \\ \mathrm{CH_3} \end{array}$$

Correct name: 2,2-dimethylpentane

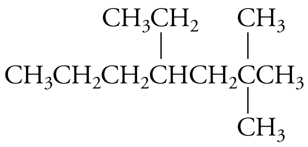
Incorrect names: 2-dimethylpentane
2,2-methylpentane
4,4-dimethylpentane

These are not all of the IUPAC rules for alkanes, but they will handle all of our needs.

■ *Common names* are still widely used for many compounds. For example, the common name of 2-methylpropane is *isobutane*.

Example 23.1
Using the IUPAC Rules to Name an Alkane

What is the IUPAC name for the following compound?



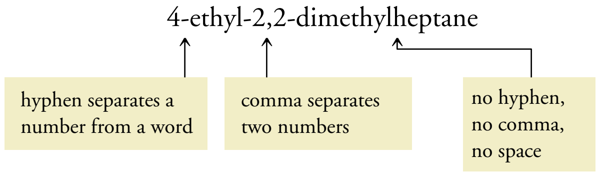
$$\begin{array}{c} \mathrm{CH_3CH_2}\quad\ \mathrm{CH_3} \\ \mathrm{CH_3CH_2CH_2\overset{|}{C}HCH_2\overset{|}{\underset{|}{C}}CH_3} \\ \mathrm{CH_3} \end{array}$$

■ **Analysis:** In naming an organic compound, the first step is to identify which family it belongs to, because the rules differ slightly according to the functional group. The compound is a hydrocarbon, and by studying the structure, we can see that there are only single bonds. Therefore, the substance is an alkane.

■ **Assembling the Tools:** Our tool, of course, is the IUPAC rules for naming alkanes.

■ **Solution:** The ending to the name must be *-ane*. The longest chain is seven carbons long, so the name of the parent alkane is *heptane*. We have to number the chain from right to left in order to reach the first branch with the lower number.

At carbon 2, there are two one-carbon methyl groups. At carbon 4, there is a two-carbon ethyl group. Alphabetically, *ethyl* comes before *methyl*, so we must assemble these names as follows to make the final name. (Names of alkyl groups are alphabetized *before* any prefixes such as di- or tri- are affixed.)


4-ethyl-2,2-dimethylheptane
hyphen separates a number from a word
comma separates two numbers
no hyphen, no comma, no space

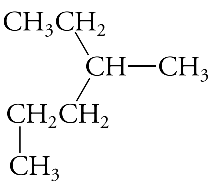
■ **Is the Answer Reasonable?** The most common mistake is to pick a shorter chain than the true "parent," a mistake we did not make. Another common mistake is to number the chain incorrectly. One overall check that some people use is to count the number of carbons implied by the name (in our example, $2 + 1 + 1 + 7 = 11$) and compare it to the count obtained directly from the structure. If the counts don't match, you know you can't be right.

Practice Exercises

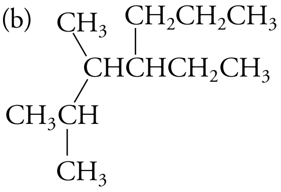
23.1 | A student incorrectly named a compound 1,1,1-trimethylethane. What should the name be? (*Hint:* Write the structure of 1,1,1-trimethylethane.)

23.2 | Write the IUPAC names of the following compounds. In searching for the parent chain, be sure to look for the longest continuous chain of carbons *even if the chain twists and goes around corners.*

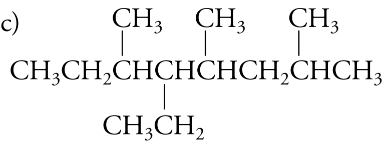
(a)



(b)



(c)



$$\begin{array}{c} \quad\quad CH_3 \quad CH_3 \quad\quad CH_3 \\ CH_3CH_2CHCHCHCH_2CHCH_3 \\ CH_3CH_2 \end{array}$$

Chemical Properties of Alkanes

Alkanes are relatively unreactive at room temperature. They do not react with concentrated acids such as H_2SO_4 or concentrated aqueous bases such as NaOH. Like all hydrocarbons, alkanes burn in air to give water and oxides of carbon (CO_2 and CO). *Hot* nitric acid, chlorine, and bromine also react with alkanes. The chlorination of methane, for example, can be made to give the following compounds:

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
methyl chloride	methylene chloride	chloroform	carbon tetrachloride

■ Halogens form single bonds to carbon atoms. These are the common names for the chlorinated derivatives of methane, not the IUPAC names.

When heated at high temperatures in the absence of air, alkanes "crack," meaning that they break up into smaller molecules. The cracking of methane, for example, yields finely powdered carbon and hydrogen.

$$CH_4 \xrightarrow{\text{high temperature}} C + 2H_2$$

The controlled cracking of ethane gives ethene, commonly called ethylene.

$$\underset{\text{ethane}}{CH_3CH_3} \xrightarrow{\text{high temperature}} \underset{\text{ethene}}{CH_2{=}CH_2} + H_2$$

Ethene ("ethylene"), from the cracking of ethane, is one of the most important raw materials in the organic chemicals industry. It is used to make polyethylene plastic items as well as ethanol and ethylene glycol (an antifreeze).

■ $HOCH_2CH_2OH$
ethylene glycol

Alkenes and Alkynes

Hydrocarbons with one or more double bonds are members of the alkene family. Open-chain alkenes have the general formula, C_nH_{2n}. Hydrocarbons with triple bonds are in the alkyne family, and have the general formula, C_nH_{2n-2} (when open-chain).

Alkenes and alkynes, like all hydrocarbons, are virtually nonpolar and therefore insoluble in water, and they are flammable. The most familiar alkenes are ethene and propene (commonly called ethylene and propylene, respectively), the raw materials for polyethylene and polypropylene, respectively. Ethyne ("acetylene"), an important alkyne, is the fuel for oxyacetylene torches.

■ The IUPAC accepts both *ethene* and *ethylene* as the name of $CH_2{=}CH_2$. The common name of propene is *propylene*, and other simple alkenes have common names as well.

$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$HC{\equiv}CH$
ethene (ethylene)	propene (propylene)	ethyne (acetylene)

IUPAC Nomenclature of Alkenes and Alkynes

TOOLS Naming alkenes and alkynes

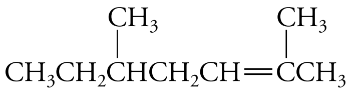
The IUPAC rules for the names of alkenes are adaptations of those for alkanes, but with two important differences. First, the parent chain *must include the double bond* even if this means that the parent chain is shorter than another. Second, the parent alkene chain must be *numbered from whichever end gives the first carbon of the double bond the lower of two possible numbers.* This (lower) number, preceded and followed by a hyphen, is inserted into name of the parent chain just before the -ene or -yne ending, unless there is no ambiguity about where the double bond occurs. The numbers for the locations of branches are not considered in numbering the chain. Otherwise, alkyl groups are named and located as before. Some examples of correctly named alkenes are as follows:

$CH_3CH_2CH{=}CH_2$

but-1-ene
(not but-3-ene)

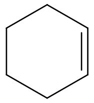
$CH_3CH{=}CHCH_3$

but-2-ene



$$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3$$

2,5-dimethylhept-2-ene
(not 3,6-dimethyl-5-heptene)



cyclohexene

Notice that only one number is used to locate the double bond, the number of the first carbon of the double bond to be reached as the chain is numbered.

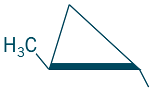
Some alkenes have two double bonds and are called *dienes*. Some have three double bonds and are called *trienes*, and so forth. Each double bond has to be located by a number.

$CH_2{=}CHCH{=}CHCH_3$	$CH_2{=}CHCH_2CH{=}CH_2$	$CH_2{=}CHCH{=}CHCH{=}CH_2$
penta-1,3-diene	penta-1,4-diene	hexa-1,3,5-triene

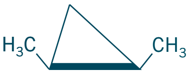
Geometric Isomerism

As explained in Section 10.6, rotation of one part of a molecule relative to another around a carbon–carbon double bond cannot occur without bond breaking (see page 440). As a result, the orientations of the atoms bonded to the carbons of the double bond are locked in place. This allows many alkenes to exhibit **geometric isomerism**. Thus, *cis*-but-2-ene and *trans*-but-2-ene (commonly called *cis*-2-butene and *trans*-2-butene, respectively) are **geometric isomers** of each other (see below). They not only have the same molecular formula, C_4H_8, but also the same skeletons and the same organization of atoms and bonds—namely, $CH_3CH{=}CHCH_3$. The two 2-butenes differ in the *directions* taken by the two CH_3 groups attached at the double bond.

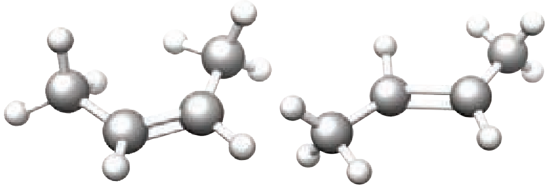
■ Because ring structures also lock out free rotation, geometric isomers of ring compounds are also possible. These two isomers of 1,2-dimethylcyclopropane are examples. In the representations below, the ring is viewed tilting back into the page, with the front edge of the ring shown as a heavy line.

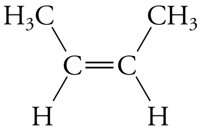


trans isomer
BP 28 °C

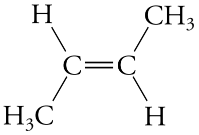


cis isomer
BP 37 °C





cis-but-2-ene
BP 3.72 °C



trans-but-2-ene
BP 0.88 °C

Cis means "on the same side;" trans means "on opposite sides." This difference in orientation gives the two geometric isomers of 2-butene measurable differences in physical properties, as their boiling points show. Because each has a double bond, however, the *chemical* properties of *cis*- and *trans*-2-butene are very similar.

Reactions of Alkenes

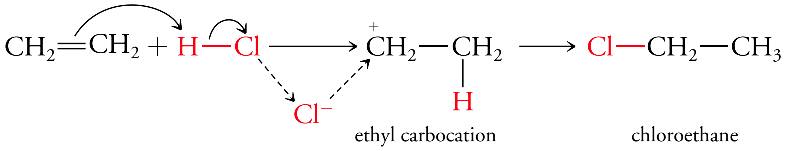
A double bond has more electron density than a single bond, so electron-seeking species such as protons are naturally attracted to the electron density at the π bond of the double bond. As a result, alkenes can react readily with protons provided by strong proton donors to give **addition reactions** in which two parts of a reactant become separately attached to the two carbons of a double bond. Ethene, for example, readily reacts with hydrogen chloride as follows:

$$CH_2{=}CH_2 + H{-}Cl(g) \longrightarrow Cl{-}CH_2{-}CH_3$$

TOOLS

Reactions of alkenes and alkynes

We say that the hydrogen chloride molecule *adds across the double bond*, the hydrogen of HCl going to the carbon at one end and the chlorine going to the other end. The pair of electrons of the π bond move out and take H^+ from HCl, which releases Cl^-. A positive (+) charge is left at one end of the original carbon–carbon double bond as a bond to H forms at the other end.

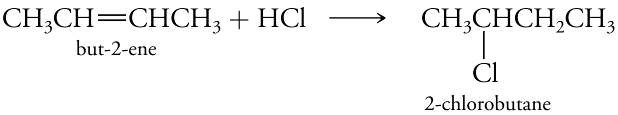


■ Recall that curved arrows indicate how electron pairs rearrange; they usually are not used to signify the movement of atoms.

The result of H^+ transfer is a very unstable cation called a *carbocation*, an ion with a positive charge on carbon. This charged site then quickly attracts the Cl^- ion to give the product, chloroethane.

■ A carbocation, having a carbon with only six valence electrons, not an octet, generally has only a fleeting existence.

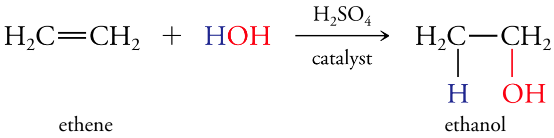
Another example is 2-butene; like ethene, it too adds HCl.



$$\underset{\text{but-2-ene}}{CH_3CH{=}CHCH_3} + HCl \longrightarrow \underset{\text{2-chlorobutane}}{\begin{array}{l}CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3\end{array}}$$

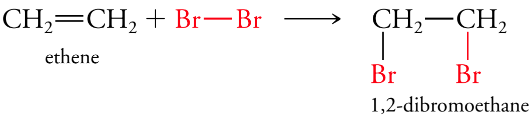
Alkene double bonds also add hydrogen bromide, hydrogen iodide, and sulfuric acid ("hydrogen sulfate"). Alkynes undergo similar addition reactions.

A water molecule adds to a double bond if an acid catalyst, like sulfuric acid, is present. The resulting product is an alcohol. For example, adding H_2O to the double bond of ethene gives ethanol as the product.



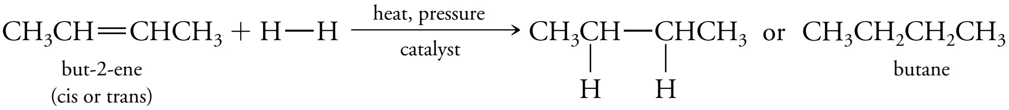
$$\underset{\text{ethene}}{H_2C{=}CH_2} + HOH \xrightarrow[\text{catalyst}]{H_2SO_4} \underset{\text{ethanol}}{\begin{array}{cc}H_2C & -CH_2\\ | & |\\ H & OH\end{array}}$$

Other inorganic compounds that add to an alkene double bond are chlorine, bromine, and hydrogen. Chlorine and bromine react rapidly at room temperature. Ethene, for example, reacts with bromine to give 1,2-dibromoethane.



$$\underset{\text{ethene}}{CH_2{=}CH_2} + Br{-}Br \longrightarrow \underset{\text{1,2-dibromoethane}}{\begin{array}{cc}CH_2 & -CH_2\\ | & |\\ Br & Br\end{array}}$$

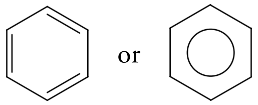
The product of the addition of hydrogen to an alkene is an alkane and the reaction is called *hydrogenation*. It requires a catalyst—powdered platinum, for example—and sometimes a higher temperature and pressure than available under an ordinary room atmosphere. The hydrogenation of 2-butene (cis or trans) gives butane.



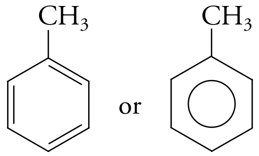
$$\underset{\substack{\text{but-2-ene}\\ \text{(cis or trans)}}}{CH_3CH{=}CHCH_3} + H{-}H \xrightarrow[\text{catalyst}]{\text{heat, pressure}} \begin{array}{cc}CH_3CH & -CHCH_3\\ | & |\\ H & H\end{array} \text{ or } \underset{\text{butane}}{CH_3CH_2CH_2CH_3}$$

Aromatic Hydrocarbons

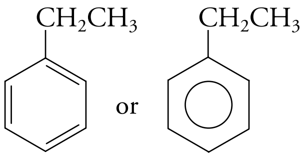
The most common **aromatic compounds** contain the *benzene ring*, a ring of six carbon atoms, each bonded to one H or one other atom or group. The benzene ring is represented as a hexagon either with alternating single and double bonds or with a circle. For example,



benzene



toluene
(methylbenzene)



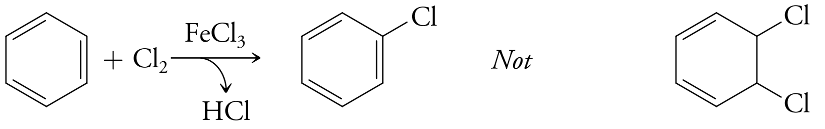
ethylbenzene

■ Hydrocarbons and their oxygen or nitrogen derivatives that are not aromatic are called *aliphatic compounds*.

The circle better suggests the delocalized bonds of the benzene ring, which are described in Section 10.8.

In the molecular orbital view of benzene, discussed in Section 10.8, the delocalization of the ring's π electrons strongly stabilizes the ring. This explains why benzene does not easily give addition reactions; they would interfere with the delocalization of electron density. Instead, the benzene ring most commonly undergoes **substitution reactions**, those in which one of the ring H atoms is replaced by another atom or group. For example, benzene reacts with chlorine in the presence of iron(III) chloride to give chlorobenzene, instead of a 1,2-dichloro compound. To dramatize this point, we must use a resonance structure for benzene (see page 452).

■ In this reaction, $FeCl_3$ is a catalyst. The HCl is a product, indicated by the second, curved arrow.



chlorobenzene

(This would form if chlorine *added* to the double bond.)

You can infer that *substitution,* but not addition, leaves intact the delocalized and very stable π electron network of the benzene ring.

Provided that a suitable catalyst is present, benzene reacts by substitution with chlorine, bromine, and nitric acid as well as with sulfuric acid. (Recall that Cl_2 and Br_2 readily *add* to alkene double bonds.)

$$C_6H_6 + Br_2 \xrightarrow{\text{FeBr}_3\text{ catalyst}} \underset{\text{bromobenzene}}{C_6H_5{-}Br} + HBr$$

$$C_6H_6 + HNO_3 \xrightarrow{\text{H}_2\text{SO}_4\text{ catalyst}} \underset{\text{nitrobenzene}}{C_6H_5{-}NO_2} + H_2O$$

$$C_6H_6 + H_2SO_4 \longrightarrow \underset{\text{benzenesulfonic acid}}{C_6H_5{-}SO_3H} + H_2O$$

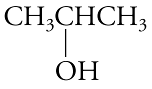
23.3 | Organic Compounds Containing Oxygen

Most of the organic compounds we encounter are not hydrocarbons, although they all contain fragments that are considered to be derived from hydrocarbons. In this section we study compounds that possess the oxygen-containing functional groups in Table 23.1.

Alcohols and Ethers

Alcohols were discussed in Chapter 9. In general, they include any compound with an OH group bonded to a carbon that is also attached to three other groups by *single bonds*. Using the symbol R to represent any alkyl group, alcohols have ROH as their general structure.

The four structurally simplest alcohols are the following (their common names are in parentheses below their IUPAC names):

CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	 $\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}$
methanol	ethanol	propan-1-ol	propan-2-ol
(methyl alcohol)	(ethyl alcohol)	(propyl alcohol)	(isopropyl alcohol)
BP 65 °C	BP 78.5 °C	BP 97 °C	BP 82 °C

Ethanol is the alcohol in beverages and is also added to gasoline to make "gasohol" and makes up 85% of the fuel E-85 (the rest is gasoline).

Molecules of **ethers** contain two alkyl groups joined to one oxygen, the two R groups being alike or different. We give only the common names for the following examples:

CH_3OCH_3	$CH_3CH_2OCH_2CH_3$	$CH_3OCH_2CH_3$	R—O—R′
dimethyl ether	diethyl ether	methyl ethyl ether	ethers
BP −23 °C	BP 34.5 °C	BP 11 °C	(general structure)

Diethyl ether is the "ether" that was once widely used as an anesthetic during surgery.

The contrasting boiling points of alcohols and ethers illustrate the influence of hydrogen bonding. Hydrogen bonds cannot exist between molecules of ethers and the simple ethers have very low boiling points, being substantially lower than those of alcohols of comparable molecular sizes. For example, 1-butanol, $CH_3CH_2CH_2CH_2OH$ (BP 117 °C) boils 83 degrees higher than its structural isomer, diethyl ether (BP 34.5 °C).

Naming Alcohols

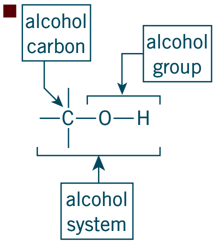
The name ending for an alcohol is *-ol*. It replaces the *-e* ending of the name of the hydrocarbon that corresponds to the parent. The parent chain of an alcohol must be the longest *that includes the carbon holding the OH group*. The chain is numbered to give the site of the OH group the lower number regardless of where alkyl substituents occur.

TOOLS

Naming alcohols

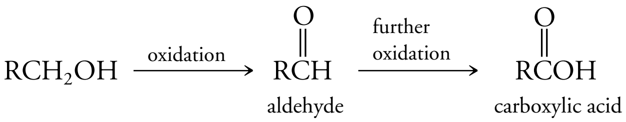
Major Reactions of Alcohols and Ethers

Ethers are almost as chemically inert as alkanes. They burn (as do alkanes), and they are split apart when boiled in concentrated acids.



The alcohols, in contrast, have a rich chemistry. When the carbon atom of the alcohol system, the *alcohol carbon atom,* is also bonded to at least one H, this H can be removed by an oxidizing agent. The H atom of the OH group will also leave, and the oxygen will form a double bond with the carbon. The two H atoms become part of a water molecule, and we may think of the oxidizing agent as providing the O atom for H_2O. At this point, the number of H atoms that remain on the original alcohol carbon then determines the *family* of the product.

The oxidation of an alcohol of the RCH_2OH type, with two H atoms on the alcohol carbon, produces first an *aldehyde*, which is further oxidized to a *carboxylic acid*. (We will say more about aldehydes and carboxylic acids later in this section.)



$$RCH_2OH \xrightarrow{\text{oxidation}} \underset{\text{aldehyde}}{\overset{\displaystyle O}{\overset{\|}{RCH}}} \xrightarrow{\text{further oxidation}} \underset{\text{carboxylic acid}}{\overset{\displaystyle O}{\overset{\|}{RCOH}}}$$

TOOLS

Oxidation of alcohols

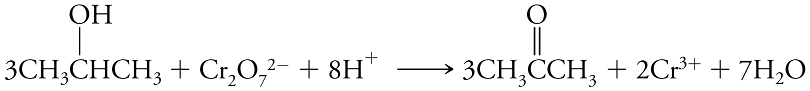
The net ionic equation for the formation of the aldehyde when dichromate ion is used is

$$3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3RCH{=}O + 2Cr^{3+} + 7H_2O$$

The aldehyde group, CH═O, is one of the most easily oxidized, and the carboxyl group, CO_2H, is one of the most oxidation resistant of the functional groups.

Aldehydes are much more easily oxidized than alcohols, so unless the aldehyde is removed from the solution as it forms, it will consume oxidizing agent that has not yet reacted and be changed to the corresponding carboxylic acid.

The oxidation of an alcohol of the R_2CHOH type produces a *ketone*. For example, the oxidation of 2-propanol gives propanone.



$$3CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3 + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + 2Cr^{3+} + 7H_2O$$

propan-2-ol

propanone
(acetone, a ketone)

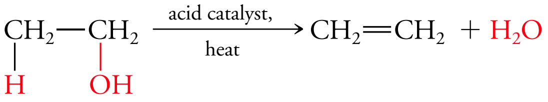
Ketones strongly resist oxidation, so a ketone does not have to be removed from the oxidizing agent as it forms.

Alcohols of the type R_3COH have no removable H atom on the alcohol carbon, so they cannot be oxidized in a similar manner.

Other Reactions of Alcohols

In the presence of a strong acid, like concentrated sulfuric acid, an alcohol molecule can undergo the loss of a water molecule, leaving behind a carbon–carbon double bond. This reaction, called **dehydration,** is one example of an **elimination reaction.** For example,

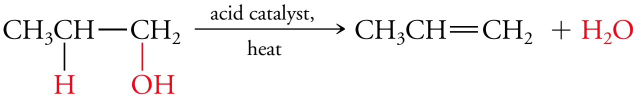
Dehydration of alcohols



$$\underset{\underset{\displaystyle H}{|}}{CH_2}{-}\underset{\underset{\displaystyle OH}{|}}{CH_2} \xrightarrow[\text{heat}]{\text{acid catalyst,}} CH_2{=}CH_2 + H_2O$$

ethanol

ethene



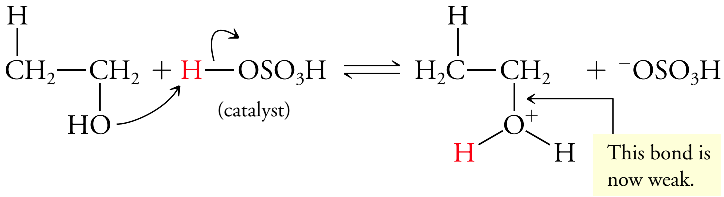
$$CH_3\underset{\underset{\displaystyle H}{|}}{CH}{-}\underset{\underset{\displaystyle OH}{|}}{CH_2} \xrightarrow[\text{heat}]{\text{acid catalyst,}} CH_3CH{=}CH_2 + H_2O$$

propan-1-ol

propene

What makes the elimination of water possible is the proton-accepting ability of the O atom of the OH group. Alcohols resemble water in that they react like Brønsted bases toward concentrated strong acids to give an equilibrium mixture involving a protonated form. Ethanol, for example, dissolves in and reacts with concentrated sulfuric acid by the following reaction (H_2SO_4 is written as $H{-}OSO_3H$):[1]

Remember: the curved arrows in these diagrams show how *electrons* rearrange during the reaction. They don't indicate the movements of the atoms.



$$\overset{\overset{\displaystyle H}{|}}{CH_2}{-}\underset{\underset{\displaystyle HO}{|}}{CH_2} + H{-}OSO_3H \rightleftharpoons \overset{\overset{\displaystyle H}{|}}{H_2C}{-}\underset{\underset{\displaystyle H\diagup O^+\diagdown H}{|}}{CH_2} + {}^-OSO_3H$$

(catalyst)

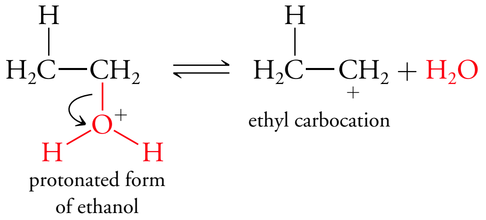
This bond is now weak.

The organic cation is nothing more than the ethyl derivative of the hydronium ion, $CH_3CH_2OH_2^+$, and *all three bonds to oxygen in this cation are weak*, just like all three bonds to oxygen in H_3O^+.

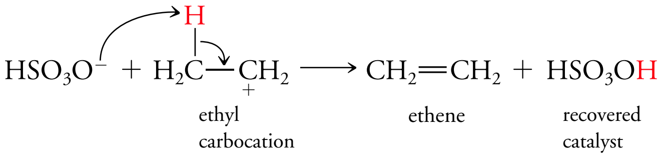
A water molecule now leaves, taking with it the electron pair that held it to the CH_2 group. The remaining organic species is a carbocation.

---

[1] The first curved arrow illustrates how an atom attached to one molecule, like the O of the HO group, uses an unshared pair of electrons to pick up an atom of another molecule, like the H of the catalyst. The second curved arrow shows that *both* electrons of the bond from H to O in sulfuric acid remain in the hydrogen sulfate ion that forms. Thus H transfers as H^+.



Carbocations are unstable. The ethyl carbocation, $CH_3CH_2^+$, loses a proton to become more stable, donating it to a proton acceptor such as HSO_3O^- to reform the catalyst HSO_3H. The electron pair that was used in the bonding to the departing proton stays behind to become the second bond of the new double bond in the product. The next equation illustrates this step. All carbon atoms now have outer octets.



The last few steps in the dehydration of ethanol—the separation of H_2O, loss of the proton, formation of the double bond, and recovery of the catalyst—probably occur simultaneously. Notice two things about the catalyst, H_2SO_4. First, it works to convert a species with strong bonds, the alcohol, to one with weak bonds strategically located, the protonated alcohol. Second, the H_2SO_4 is recovered, as it must be if it is to be considered a catalyst.

Under acidic conditions, the OH group of an alcohol can be *replaced* by a halogen atom using a concentrated strong binary acid. For example,

Substitution reactions of alcohols

$$CH_3CH_2OH + HI(conc.) \xrightarrow{heat} CH_3CH_2I + H_2O$$

ethanol — iodoethane (ethyl iodide)

$$CH_3CH_2CH_2OH + HBr(conc.) \xrightarrow{heat} CH_3CH_2CH_2Br + H_2O$$

propan-1-ol — 1-bromopropane (propyl bromide)

These reactions, like that between chlorine and benzene in Section 23.2, are **substitution reactions.** The first step in each is the transfer of H^+ to the OH of the alcohol to give the protonated form of the OH group.

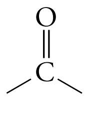
$$R{-}OH + H^+ \longrightarrow R{-}OH_2^+$$

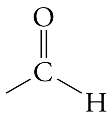
The acid catalyst works to weaken the R—O bond in R—OH by adding H^+ to form $R{-}OH_2^+$. Given the high concentration of halide ion, X^-, it is this species that successfully reacts with $R{-}OH_2^+$ to displace OH_2 (H_2O) and yield R—*X*.

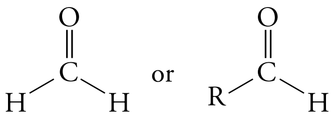
Aldehydes and Ketones

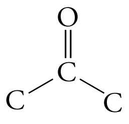
In Chapter 9 we described the **carbonyl group,** $>C{=}O$, and noted its presence in aldehydes and ketones, and we've seen how these compounds are formed in the oxidation of alcohols.

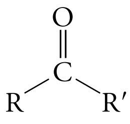
What differentiates aldehydes from ketones are the atoms attached to the carbon of the C═O group. When the carbon atom of the carbonyl group binds an H atom plus a hydrocarbon group (or a second H), the compound is an *aldehyde*. When C═O is bonded to two hydrocarbon groups at C, the compound is a *ketone*.


carbonyl group


aldehyde group


aldehydes


keto group


ketones

The *aldehyde group* is often condensed to CHO, the double bond of the carbonyl group being "understood." The *ketone group* (or *keto* group) is sometimes similarly condensed to CO.

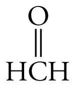
The polar carbonyl group can participate in hydrogen bonding, which helps to make compounds containing it much more soluble in water than hydrocarbons of roughly the same molecular size.

The carbonyl group occurs widely. As an aldehyde group, it's in the molecules of most sugars, like glucose. Another common sugar, fructose, has the keto group.

Naming Aldehydes and Ketones

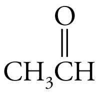
Naming aldehydes and ketones

The IUPAC name ending for an aldehyde is *-al*. The parent chain is the longest chain *that includes the aldehyde group*. Thus, the three-carbon aldehyde is named *propanal*, because "propane" is the name of the three-carbon alkane and the *-e* in propane is replaced by *-al*. Because, by definition, the aldehyde group must be at the end of a chain, the numbering of the chain always starts by assigning the carbon of the aldehyde group position 1. This rule makes it unnecessary to include the number locating the aldehyde group in the name, as illustrated by the name 2-methylpropanal.



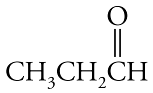
$H\overset{\overset{O}{\|}}{C}H$

methanal
BP −21 °C



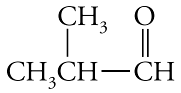
$CH_3\overset{\overset{O}{\|}}{C}H$

ethanal
BP 21 °C



$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

propanal
BP 49 °C



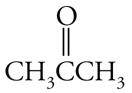
$CH_3\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{O}{\|}}{C}H$

2-methylpropanal
(not 2-methyl-1-propanal)
BP 64 °C

Aldehydes cannot form hydrogen bonds between their own molecules, so they boil at lower temperatures than alcohols of comparable molecular size.

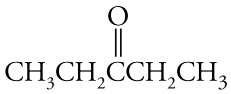
The name ending for the IUPAC names of ketones is *-one*. The parent chain must include the carbonyl group and be numbered from whichever end reaches the carbonyl carbon first. The number of the ketone group's location must be part of the name whenever there would otherwise be uncertainty.

■ We need not write "propan-2-one," because if the carbonyl carbon is anywhere else in a three-carbon chain, the compound could not be a ketone; it would be the *aldehyde*, propanal.



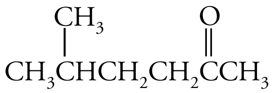
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

propanone
(acetone)
BP 56.5 °C



$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

pentan-3-one
BP 101.5 °C



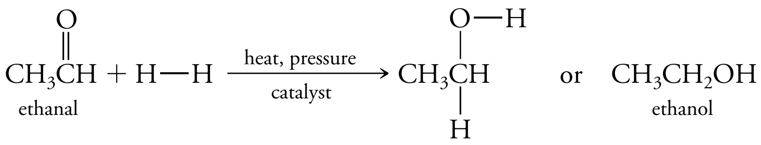
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

5-methylhexan-2-one
(not 2-methylhexan-5-one)
BP 145 °C

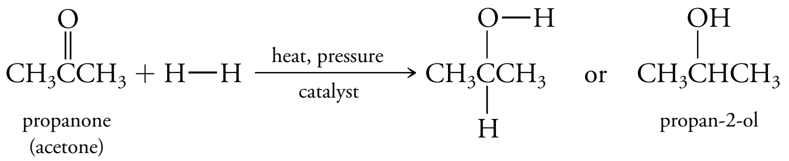
Reactions of Aldehydes and Ketones

Hydrogen is capable of adding across the double bond of the carbonyl group in both aldehydes and ketones. The reaction is just like the addition of hydrogen across the double bond of an alkene and takes place under roughly the same conditions—namely, with a metal catalyst, heat, and pressure. The reaction is called either *hydrogenation* or *reduction*. For example,

Reduction of aldehydes and ketones



$$CH_3\overset{\overset{O}{\|}}{C}H + H{-}H \xrightarrow[\text{catalyst}]{\text{heat, pressure}} CH_3\underset{\underset{H}{|}}{\overset{\overset{O-H}{|}}{C}}H \quad \text{or} \quad CH_3CH_2OH$$



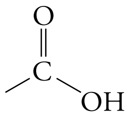
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + H{-}H \xrightarrow[\text{catalyst}]{\text{heat, pressure}} CH_3\underset{\underset{H}{|}}{\overset{\overset{O-H}{|}}{C}}CH_3 \quad \text{or} \quad CH_3\overset{\overset{OH}{|}}{C}HCH_3$$

The H atoms take up positions at opposite ends of the carbonyl group's double bond, which then becomes a single bond holding an OH group.

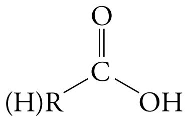
Aldehydes and ketones are in separate families because of their remarkably different behavior toward oxidizing agents. As we noted on page 1062, aldehydes are easily oxidized, but ketones strongly resist oxidation. Even in storage in a bottle, aldehydes are slowly oxidized by the oxygen of the air trapped in the bottle.

Carboxylic Acids and Esters

A **carboxylic acid** carries an OH on the carbon of the carbonyl group.



carboxyl
group



carboxylic
acids

In condensed formulas the **carboxyl group** is often written as CO_2H (or sometimes COOH).

The name ending of the IUPAC names of carboxylic acids is *-oic acid.* The parent chain must be the longest that includes the carboxyl carbon, which is numbered position 1. The name of the hydrocarbon with the same number of carbons as the parent is then changed by replacing the terminal *-e* with *-oic acid.* For example,

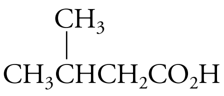
Naming organic acids

HCO_2H

methanoic acid
(formic acid)
BP 101 °C

CH_3CO_2H

ethanoic acid
(acetic acid)
BP 118 °C



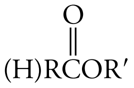
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CO_2H$$

3-methylbutanoic acid
BP 176 °C

■ Because carboxylic acids have both a lone oxygen and an OH group, their molecules strongly hydrogen bond to each other. Their high boiling points, relative to alcohols of comparable molecular size, reflect this.

Carboxylic acids are used to synthesize two important kinds of derivatives, *esters* and *amides* (which are discussed in the next section). In **esters,** the OH of the carboxyl group is replaced by OR. (The H in parentheses means the group attached to the C of the carboxyl group can either be R or H.)

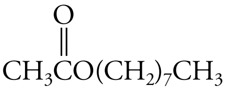
■ A *derivative* of a carboxylic acid is a compound that can be made from the acid, or can be changed to the acid by hydrolysis.



$$(H)R\overset{O}{\overset{\|}{C}}OR' \quad \text{or} \quad (H)RCO_2R',$$

esters

for example,



$$CH_3\overset{O}{\overset{\|}{C}}O(CH_2)_7CH_3$$

octyl ethanoate
(fragrance of oranges)

The IUPAC name of an ester begins with the name of the alkyl group attached to the O atom. This is followed by a separate word, which is taken from the name of the parent carboxylic acid by changing *-ic acid* to *-ate*. For example,

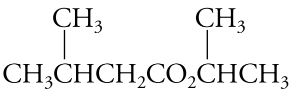
Naming esters

HCO_2CH_3

methyl methanoate
BP 31.5 °C

$CH_3CO_2CH_2CH_3$

ethylpropanoate
BP 99 °C



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CO_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

isopropyl 3-methylbutanoate
BP 142 °C

Reactions of Carboxylic Acids and Esters

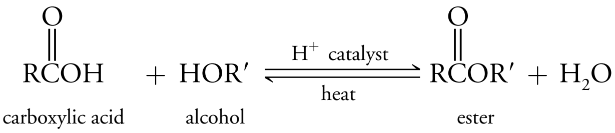
The carboxyl group is weakly acidic, causing compounds that contain it to be weak acids in water. In fact, we've used both formic acid and acetic acid in previous discussions of weak acids. All carboxylic acids, both water soluble and water insoluble, neutralize Brønsted bases such as the hydroxide, bicarbonate, and carbonate ions. The general equation for the reaction with OH^- is

$$RCO_2H + OH^- \xrightarrow{H_2O} RCO_2^- + H_2O$$

Reactions of organic acids

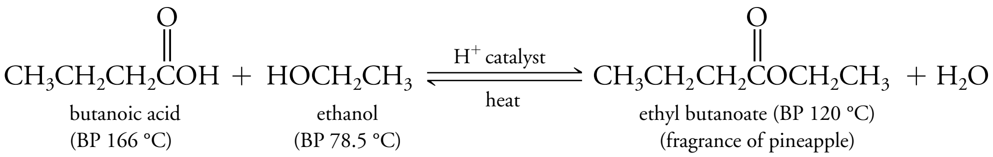
The carboxyl group is present in all of the building blocks of proteins, the amino acids, which are discussed further on page 1083.

One way to prepare an ester is to heat a solution of the parent carboxylic acid and the alcohol in the presence of an acid catalyst. (We'll not go into the details of how this happens.) The following kind of equilibrium forms, but a substantial stoichiometric excess of the alcohol (usually the less expensive reactant) is commonly used to drive the position of the equilibrium toward the ester.



$$\underset{\text{carboxylic acid}}{\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}} + \underset{\text{alcohol}}{\mathrm{HOR'}} \xrightleftharpoons[\text{heat}]{\mathrm{H^+}\ \text{catalyst}} \underset{\text{ester}}{\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'}} + \mathrm{H_2O}$$

For example,



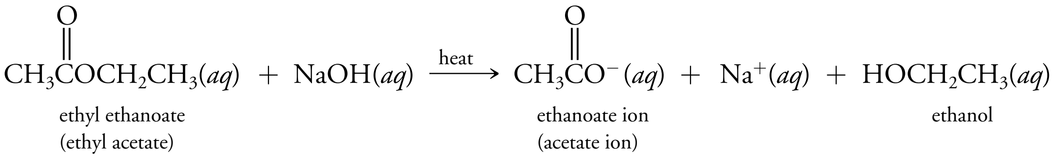
$$\underset{\substack{\text{butanoic acid}\\ \text{(BP 166 °C)}}}{\mathrm{CH_3CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}} + \underset{\substack{\text{ethanol}\\ \text{(BP 78.5 °C)}}}{\mathrm{HOCH_2CH_3}} \xrightleftharpoons[\text{heat}]{\mathrm{H^+}\ \text{catalyst}} \underset{\substack{\text{ethyl butanoate (BP 120 °C)}\\ \text{(fragrance of pineapple)}}}{\mathrm{CH_3CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_3}} + \mathrm{H_2O}$$

An ester is hydrolyzed to its parent acid and alcohol when the ester is heated together with a stoichiometric excess of water (plus an acid catalyst). The identical equilibrium as shown above forms, but in ester hydrolysis water is in excess, so the equilibrium shifts to the left to favor the carboxylic acid and alcohol, another illustration of Le Châtelier's principle.

TOOLS

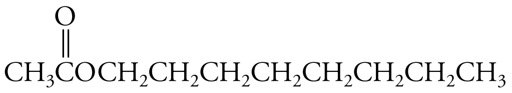
Saponification of esters

Esters are also split apart by the action of aqueous base, only now the carboxylic acid emerges not as the free acid but as its anion. The reaction is called ester **saponification**. We can illustrate it by the action of aqueous sodium hydroxide on ethyl ethanoate, a simple ester:



$$\underset{\substack{\text{ethyl ethanoate}\\ \text{(ethyl acetate)}}}{\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_3}(aq)} + \mathrm{NaOH}(aq) \xrightarrow{\text{heat}} \underset{\substack{\text{ethanoate ion}\\ \text{(acetate ion)}}}{\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O^-}(aq)} + \mathrm{Na^+}(aq) + \underset{\text{ethanol}}{\mathrm{HOCH_2CH_3}(aq)}$$

Ester groups abound among the molecules of the fats and oils in our diets. The hydrolysis of their ester groups occurs when we digest them, with an enzyme as the catalyst, not a strong acid. Because this digestion occurs in a region of the intestinal tract where the fluids are slightly basic, the anions of carboxylic acids form. Esters also tend to have pleasant aromas and are responsible for the fragrance of many fruits. For example, octyl acetate,



$$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3}$$

octyl acetate

gives oranges their characteristic odor. See the table in the margin.

Ester	**Aroma**
$HCO_2CH_2CH_3$	Rum
$HCO_2CH_2CH(CH_3)_2$	Raspberries
$CH_3CO_2(CH_2)_4CH_3$	Bananas
$CH_3CO_2(CH_2)_2CH(CH_3)_2$	Pears
$CH_3CO_2(CH_2)_7CH_3$	Oranges
$CH_3(CH_2)_2CO_2CH_2CH_3$	Pineapples
$CH_3(CH_2)_2CO_2(CH_2)_4CH_3$	Apricots

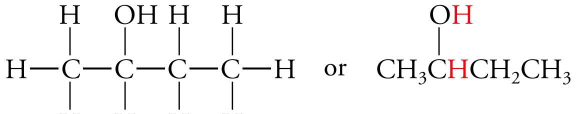
Example 23.2
Alcohol Oxidation Products

What is the structure of the organic product made by the oxidation of butan-2-ol with dichromate ion? If no oxidation can occur, so state.

Analysis: We first have to determine the structure of butan-2-ol. The oxidation product then depends on the number of hydrogens attached to the alcohol carbon atom.

Assembling the Tools: First, we have to use the nomenclature rules to draw the structure of butan-2-ol. If there are no H atoms on the alcohol carbon, oxidation by dichromate ion cannot occur. If there is one H atom on the alcohol carbon, the tool we use predicts that the product will be a ketone. If there are two H atoms on the alcohol carbon, the product will be an aldehyde.

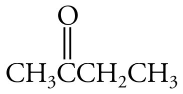
Solution: The nomenclature rules tell us that the OH group of the alcohol is on carbon number 2 of a four-carbon chain of singly bonded carbon atoms. In drawing the structure we have to remember that each carbon atom must have four bonds.



$$\begin{array}{c} H\quad OH\quad H\quad H \\ H-\underset{H}{C}-\underset{H}{C}-\underset{H}{C}-\underset{H}{C}-H \end{array} \quad \text{or} \quad CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3$$

butan-2-ol

The alcohol carbon has one H atom, so the product will be a ketone. The oxidation results in the detachment of both the H atom on the alcohol carbon (carbon 2) and the one joined to the O atom of the OH group, leaving a double bond to O. We simply erase the two H atoms shown in red and insert a double bond from C to O. (The product is called *butanone*.)



$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$$

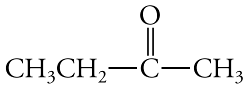
butanone (a ketone)

Is the Answer Reasonable? The starting material had two alkyl groups, CH_3 and CH_2CH_3. It doesn't matter what these alkyl groups are, however, because the reaction takes the same course in all cases. All alcohols of the R_2CHOH type can be oxidized to ketones in this way.

The "skeleton" of heavy atoms, C and O, does not change in this kind of oxidation, and butanone has the same skeleton as butan-2-ol. The oxidation also produces a double bond from C to O, as we showed.

Practice Exercises

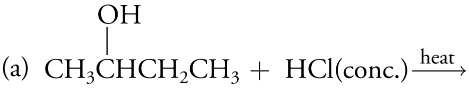
23.3 | Oxidation of an alcohol gave the following product. What was the formula of the original alcohol? (*Hint:* How many hydrogens are removed from the alcohol carbon by oxidation?)



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

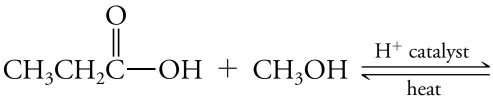
23.4 | What are the structures of the products (if any) that form from the oxidation of the following alcohols by dichromate ion? (a) ethanol, (b) pentan-3-ol, (c) 2-methylpropan-2-ol

23.5 | Write the structural formula(s) for the principal organic product(s) in the following reactions:



(a) $CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3 + HCl(conc.) \xrightarrow{heat}$ (b) $CH_3CH_2CH_2OH \xrightarrow[Conc.]{H_2SO_4}$

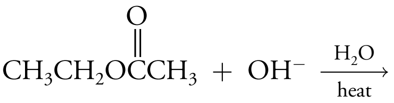
23.6 | Complete the following equation and write the structural formula for the principal organic product. What is the name of the product?



$$CH_3CH_2\overset{\overset{O}{\|}}{C}-OH + CH_3OH \underset{heat}{\overset{H^+ \text{ catalyst}}{\rightleftharpoons}}$$

23.7 | Write structural formulas for the following: (a) 3-methylbutanal, (b) ethyl propionate, and (c) butanone.

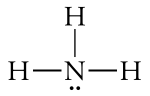
23.8 | Write the structural formula(s) for the principal organic product(s) in the following reaction:



$$CH_3CH_2O\overset{\overset{O}{\|}}{C}CH_3 + OH^- \xrightarrow[heat]{H_2O}$$

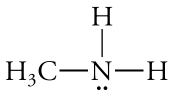
23.4 | Organic Derivatives of Ammonia

As described in Chapter 9, **amines** can be viewed as organic derivatives of ammonia in which one, two, or three hydrocarbon groups have replaced hydrogens. Examples, together with their common (not IUPAC) names, are



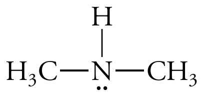
$$\mathrm{H{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}H}$$

ammonia
BP −33.4 °C



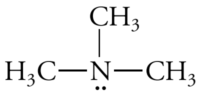
$$\mathrm{H_3C{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}H}$$

methylamine
BP −8 °C



$$\mathrm{H_3C{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}CH_3}$$

dimethylamine
BP 8 °C



$$\mathrm{H_3C{-}\overset{CH_3}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}CH_3}$$

trimethylamine
BP 3 °C

■ The following are in the order of decreasing strengths of intermolecular attractions.

CH_3CH_2OH, BP 78.5 °C

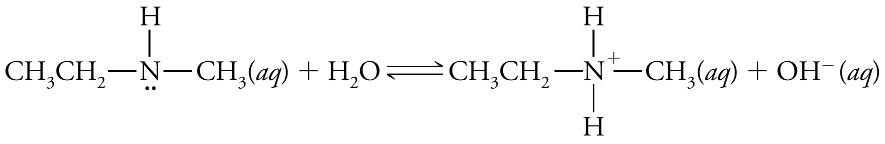
$CH_3CH_2NH_2$, BP 17 °C

$CH_3CH_2CH_3$, BP −42 °C

The N—H bond is not as polar as the O—H bond, so hydrogen bonding is not as strong and amines boil at lower temperatures than alcohols of comparable molecular size. Amines of low molecular mass are soluble in water. Hydrogen bonding between molecules of water and the amine facilitates the solution process.

Basicity and Reactions of Amines

On page 376, amines were described as weak Brønsted bases. Behaving like ammonia, amines that are able to dissolve in water establish an equilibrium in which a low concentration of hydroxide ion exists. For example,

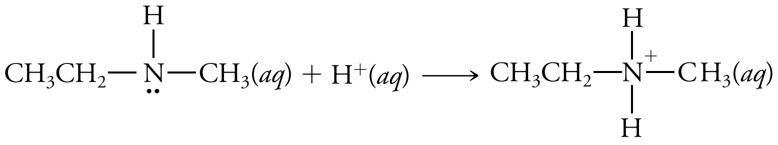


$$\mathrm{CH_3CH_2{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}CH_3}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N^+}}{-}CH_3}(aq) + \mathrm{OH^-}(aq)$$

ethylmethylamine ethylmethylammonium ion

As a result, aqueous solutions of amines test basic to litmus and have pH values above 7.

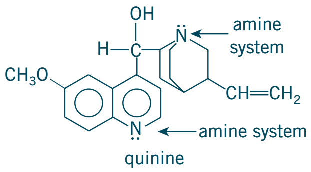
When an amine is mixed with a strong acid such as hydrochloric acid, the amine and acid react almost quantitatively. The amine accepts a proton and changes almost entirely into its protonated form. For example,



$$\mathrm{CH_3CH_2{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{N}}}{-}CH_3}(aq) + \mathrm{H^+}(aq) \longrightarrow \mathrm{CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N^+}}{-}CH_3}(aq)$$

ethylmethylamine ethylmethylammonium ion
(a protonated amine)

■



quinine
(an antimalarial drug)

Even water-insoluble amines undergo this reaction and the resulting salt is much more soluble in water that the original electrically neutral amine.

Many important medicinal chemicals, like quinine (which is used to treat malaria), are amines, but they are usually supplied to patients in protonated forms so that the drug can be administered as an aqueous solution, not as a solid. This strategy is particularly important for medicinals that must be given by intravenous drip.

Protonated Amines as Weak Brønsted Acids

A protonated amine is a substituted ammonium ion. Like the ammonium ion itself, protonated amines are weak Brønsted acids. They can neutralize strong base. For example,

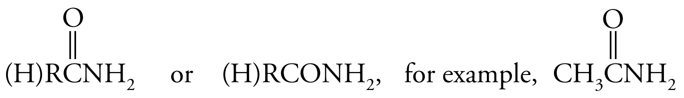
$$\mathrm{CH_3NH_3^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{CH_3NH_2}(aq) + \mathrm{H_2O}$$

methylammonium ion methylamine

This reverses the protonation of an amine and releases the uncharged amine molecule.

Amides: Derivatives of Carboxylic Acids

Carboxylic acids can also be converted to *amides*, a functional group found in proteins. In **amides,** the OH of the carboxyl group is replaced by nitrogen, which may also be bonded to any combination of H atoms or hydrocarbon groups.



$$(H)R\overset{\overset{O}{\|}}{C}NH_2 \quad \text{or} \quad (H)RCONH_2, \quad \text{for example,} \quad CH_3\overset{\overset{O}{\|}}{C}NH_2$$

simple amides

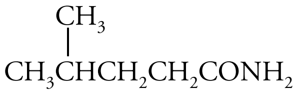
ethanamide (acetamide)

The *simple amides* are those in which the nitrogen bears no hydrocarbon groups, only two H atoms. In the place of either or both of these H atoms, however, there can be a hydrocarbon group, and the resulting substance is still an amide.

The IUPAC names of the simple amides are devised by first writing the name of the parent carboxylic acid. Then its ending, *-oic acid*, is replaced by *-amide*. For example,

$CH_3CH_2CONH_2$ propanamide

$CH_3CH_2CH_2CH_2CONH_2$ pentanamide

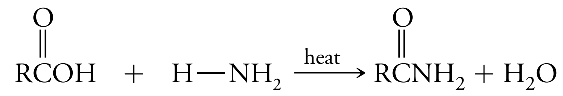


$$CH_3\underset{}{\overset{\overset{CH_3}{|}}{C}}HCH_2CH_2CONH_2$$

4-methylpentanamide

One of the ways to prepare simple amides parallels that of the synthesis of esters—that is, by heating a mixture of the carboxylic acid and an excess of ammonia.

In general:

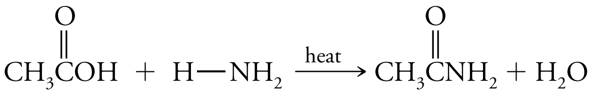


$$R\overset{\overset{O}{\|}}{C}OH + H{-}NH_2 \xrightarrow{\text{heat}} R\overset{\overset{O}{\|}}{C}NH_2 + H_2O$$

carboxylic acid ammonia simple amide

TOOLS Formation of amides

An example:

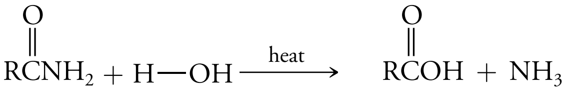


$$CH_3\overset{\overset{O}{\|}}{C}OH + H{-}NH_2 \xrightarrow{\text{heat}} CH_3\overset{\overset{O}{\|}}{C}NH_2 + H_2O$$

ethanoic acid ammonia ethanamide

Amides, like esters, can be hydrolyzed. When simple amides are heated with water, they change back to their parent carboxylic acids and ammonia. Both strong acids and strong bases promote the reaction. As the following equations show, the reaction is the reverse of the formation of an amide.

In general:

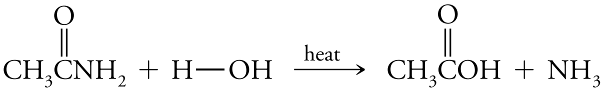


$$R\overset{\overset{O}{\|}}{C}NH_2 + H{-}OH \xrightarrow{\text{heat}} R\overset{\overset{O}{\|}}{C}OH + NH_3$$

simple amide carboxylic acid

TOOLS Hydrolysis of an amide

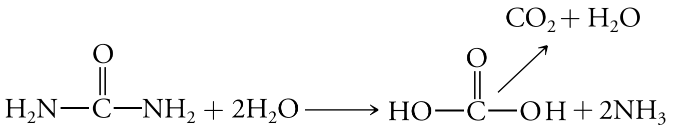
An example:



$$CH_3\overset{\overset{O}{\|}}{C}NH_2 + H{-}OH \xrightarrow{\text{heat}} CH_3\overset{\overset{O}{\|}}{C}OH + NH_3$$

ethanamide ethanoic acid

Urea, excreted in urine, is the amide of carbonic acid, H_2CO_3, and when it is hydrolyzed the products are ammonia and carbon dioxide (formed in the decomposition of H_2CO_3).



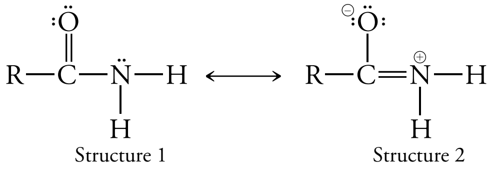
$$H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + 2H_2O \longrightarrow HO{-}\overset{\overset{O}{\|}}{C}{-}OH + 2NH_3 \qquad (\nearrow CO_2 + H_2O)$$

urea carbonic acid

This reaction explains why a baby's wet diaper gradually develops the odor of ammonia. Urea is used commercially as a fertilizer because its hydrolysis in the soil releases ammonia, a good source of nitrogen for plants.

Nonbasicity of Amides

Despite the presence of the NH_2 group in simple amides, the amides are not Brønsted bases like amines or ammonia. This can be understood by examining the following two resonance structures:



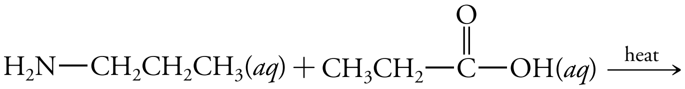
$$R-\overset{\overset{\displaystyle :\ddot{O}}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\ddot{N}}-H \longleftrightarrow R-\overset{\overset{\displaystyle ^{\ominus}:\ddot{O}:}{|}}{C}=\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{N}}-H$$

Structure 1 Structure 2

Effectively, the lone pair on the nitrogen in Structure 1 becomes partially delocalized onto the oxygen, as shown in Structure 2. This makes the lone pair on the amide nitrogen less available for donation to an H^+ than the corresponding lone pair on the nitrogen of an amine. As a result, the amide nitrogen has little tendency to acquire a proton, so amides are neutral compounds in an acid–base sense.

Practice Exercises

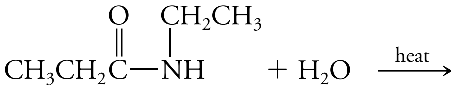
23.9 | Complete the following equation by drawing structural formulas for the products.



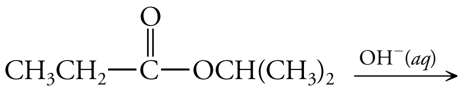
$$H_2N-CH_2CH_2CH_3(aq) + CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH(aq) \xrightarrow{\text{heat}}$$

(*Hint:* Identify the functional groups and their properties.)

23.10 | Write the structural formula(s) for the principal organic product(s) in the following reactions:

(a) 

$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}H + H_2O \xrightarrow{\text{heat}}$$

(b) 

$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH(CH_3)_2 \xrightarrow{OH^-(aq)}$$

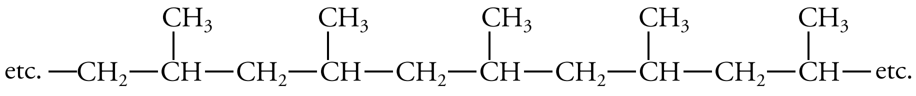
(c) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Conc.}]{H_2SO_4}$

23.5 | Organic Polymers

Nearly all of the compounds that we've studied so far are composed of relatively small molecules. Many of the substances we encounter in the world around us, however, are composed of **macromolecules**—molecules made up of hundreds or even thousands of atoms. In nature, substances with macromolecules are almost everywhere you look. They include the fibers that give strength to trees and things made of wood, and they include proteins and the DNA found in all living creatures. Macromolecules of biological origin are discussed in Section 23.6; in this section we look at synthetic macromolecules, such as those found in plastics and synthetic fibers.

Order within Polymer Molecules

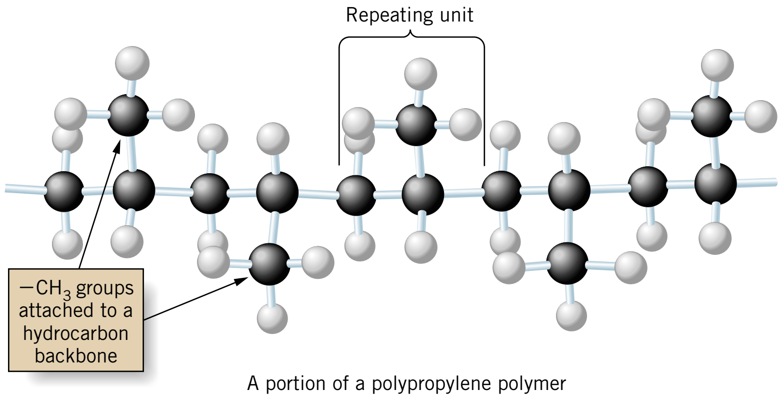
A **polymer** is a macromolecular substance whose molecules all have a small characteristic structural feature that repeats itself over and over. An example is *polypropylene*, a polymer with many uses, including dishwasher-safe food containers, indoor-outdoor carpeting, and artificial turf. The molecules of polypropylene have the following general structure:



$$\text{etc.}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\text{etc.}$$

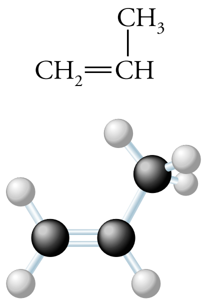
polypropylene

Notice that the polymer consists of a long carbon chain (the polymer's **backbone**) with CH_3 groups attached at periodic intervals.[2]



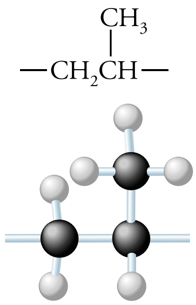
A portion of a polypropylene polymer

If you study this structure, you can see that one structural unit occurs repeatedly (actually thousands of times). In fact, the structure of a polymer is usually represented by the use of only its repeating unit, enclosed in parentheses, with a subscript *n* standing for several thousand units.



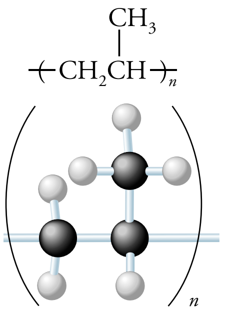
$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{CH}}$$

propylene



$$-CH_2\overset{\displaystyle CH_3}{\overset{|}{CH}}-$$

repeating unit
in polypropylene



$$\left(CH_2\overset{\displaystyle CH_3}{\overset{|}{CH}}\right)_n$$

polypropylene

The value of *n* is not a constant for every molecule in a given polymer sample. A polymer, therefore, does not consist of molecules identical in *size*, just identical in *kind*; they have the same repeating unit. Notice that despite the *-ene* ending (which is used in naming alkenes), "polypropylene" has no double bonds. The polymer is named after its starting material, propylene (IUPAC name, propene).

The repeating unit of a polymer is contributed by a chemical raw material called a **monomer**. Thus propylene is the monomer for polypropylene. The reaction that makes a polymer out of a monomer is called **polymerization**, and the verb is "to polymerize." Most (but not all) useful polymers are formed from monomers that are considered to be organic compounds.

---

[2] The drawing of the molecule shows one way the CH_3 groups can be oriented relative to the backbone and each other. Other orientations are also possible, and they affect the physical properties of the polymer.

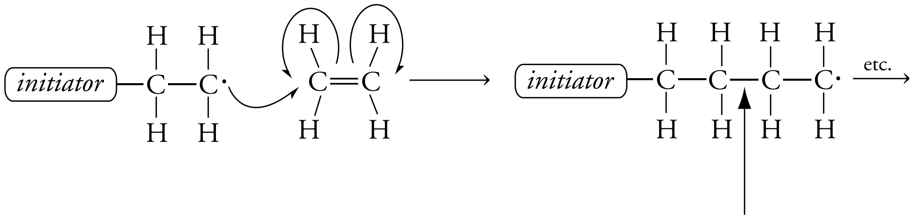
Chain-Growth Polymers

There are basically two ways that monomers become joined to form polymers—addition and condensation. In the simple addition of one monomer unit to another, the process continues over and over until a very long chain of monomer units is produced. Polymers formed by this process are called **chain-growth polymers** or **addition polymers.** Polypropylene, discussed previously, is an example of a chain-growth polymer, as is *polyethylene*, formed from ethylene ($CH_2{=}CH_2$) monomer units. Under the right conditions and with the aid of a substance called an *initiator*, a pair of electrons in the carbon–carbon double bond of ethylene becomes unpaired. The initiator binds to one carbon, leaving an unpaired electron on the other carbon. The result is a very reactive substance called a *free radical*, which can attack the double bond of another ethylene. In the attack, one of the electron pairs of the double bond becomes unpaired. One of the electrons becomes shared with the unpaired electron of the free radical, forming a bond that joins the two hydrocarbon units together. The other unpaired electron moves to the end of the chain, as illustrated in the following reaction sequence:

Addition polymerization

As the free radical approaches the ethylene molecule...

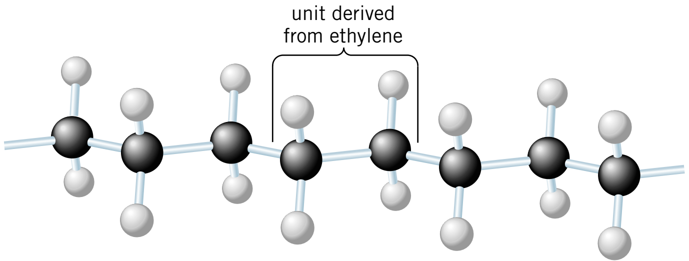
...electrons in one of the bonds unpair and move to opposite ends of the molecule.



A bond forms between the two hydrocarbon units and the unpaired electron moves to the end of the chain.

This process is repeated over and over as a long hydrocarbon chain grows. Eventually the chain becomes terminated and the result is a polyethylene molecule. The molecule is so large that the initiator, which is still present at one end of the chain, is an insignificant part of the whole, so in writing the structure of the polymer, the initiator is generally ignored.

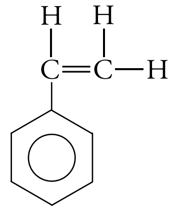
■ Actually, after ethylene has polymerized, the repeating unit in polyethylene is simply CH_2.



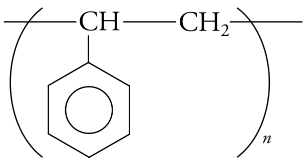
A portion of a polyethylene molecule. Although formed from a monomer with the formula C_2H_4, the actual repeating unit is CH_2.

The process by which the polymer forms has a significant influence on its ultimate structure. For example, the least expensive method for making polyethylene leads to **branching**, which means that polymer chains grow off the main backbone of the molecule as it grows longer. Other, more expensive procedures produce molecules without branching, which has a significant impact on the properties of the polymer.

In addition to polyethylene and polypropylene, another very common chain-growth polymer, called **polystyrene**, is formed by polymerizing styrene,



styrene ($C_6H_5—CH═CH_2$)



polystyrene

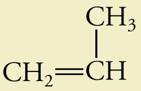
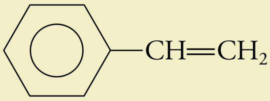
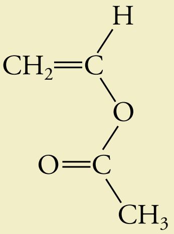
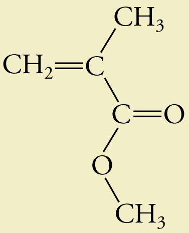
Notice that styrene is similar to propylene, but with a benzene ring in place of the methyl group ($—CH_3$). Therefore, in the polymer we find $C_6H_5—$ attached to every other atom in the hydrocarbon backbone. Polystyrene has almost as many applications as polyethylene. It's used to make clear plastic drinking glasses, molded car parts, and housings of things like computers and kitchen appliances. Sometimes a gas, like carbon dioxide, is blown through molten polystyrene as it is molded into articles. As the hot liquid congeals, tiny pockets of gas are trapped, and the product is a foamed plastic, like the familiar Styrofoam® cups or insulation materials (Figure 23.3).

Hundreds of substances similar to ethylene, propylene, and styrene, as well as their halogen derivatives, have been tested as monomers, and Table 23.3 lists some examples.

Figure 23.3 | **Styrofoam.** Made of polystyrene, Styrofoam is widely used as an insulation in construction. *(Dennis MacDonald/ PhotoEdit)*

■ A "halogen derivative" is a compound in which one or more halogen atoms substitute for hydrogens in a parent molecule. Thus, CH_3Cl is halogen derivative of CH_4.

Table 23.3 Some Addition Polymers Formed from Compounds Related to Ethylene, $CH_2═CH_2$

Polymer	Monomer	Uses
Polyethylene	$CH_2═CH_2$	Grocery bags, bottles, children's toys, bullet-proof vests
Polypropylene	 $CH_2═\overset{CH_3}{CH}$	Dishwasher-safe plastic kitchenware, indoor-outdoor carpeting, rope
Polystyrene		Plastic cups, toys, housings for kitchen appliances, Styrofoam insulation
Polyvinyl chloride (PVC)	$CH_2═CHCl$	Insulation, credit cards, vinyl siding for houses, bottles, plastic pipe
Polytetrafluoroethylene (Teflon)	$F_2C═CF_2$	Nonstick surfaces on cookware, valves
Polyvinyl acetate (PVA)		Latex paint, coatings, glue, molded items
Polymethyl methacrylate (Lucite)		Shatter-resistant windows, coatings, acrylic paints, molded items

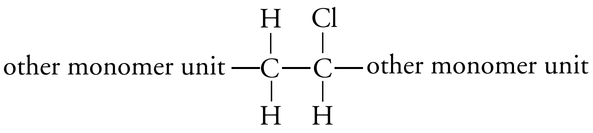
Example 23.3
Writing the Formula for a Chain-Growth Polymer

Use the information in Table 23.3 to write the structure of the polymer polyvinyl chloride showing three repeat units. Write the general formula for this polymer.

Analysis: The polymer we're dealing with is a chain-growth polymer, so we can anticipate that the entire $CH_2{=}CHCl$ molecule will repeat over and over. The polymer will be formed by opening the double bond, as we saw for ethylene.

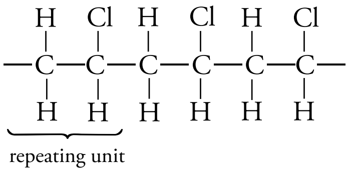
Assembling the Tools: The tool we use to solve the problem is the method by which monomer units add to each other in the formation of the polymer.

Solution: When the double bond opens, bonds to two other monomer units will form.



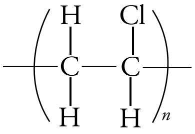
$$\text{other monomer unit}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\text{other monomer unit}$$

We need to attach three repeating units to have the answer to the problem.



$$\underbrace{-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}}_{\text{repeating unit}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-$$

The general formula for the polymer should indicate the repeating unit occurring *n* times.



$$-\!\left(\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\right)_{\!n}\!-$$

Is the Answer Reasonable? There's not much to check here, other than to be sure that the repeating unit has the same molecular formula as the monomer, which it does.

Practice Exercises

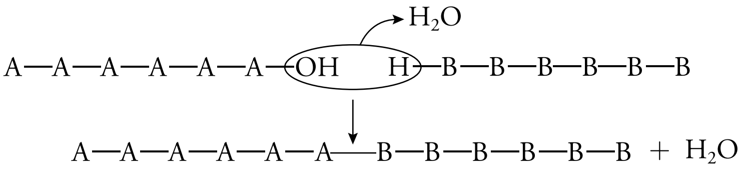
23.11 | Suppose but-2-ene were polymerized. Make a sketch showing three repeating units of the monomer in the polymer. (*Hint:* What is the structure of but-2-ene?)

23.12 | Write a formula showing three repeating units of the monomer in the polymer Teflon. (See Table 23.3.)

Step-Growth Polymers

The second way that monomer units can combine to form a polymer is by a process called **condensation**, in which a small molecule is eliminated when the two monomer units become joined. In a simplified way, we can diagram this as follows.

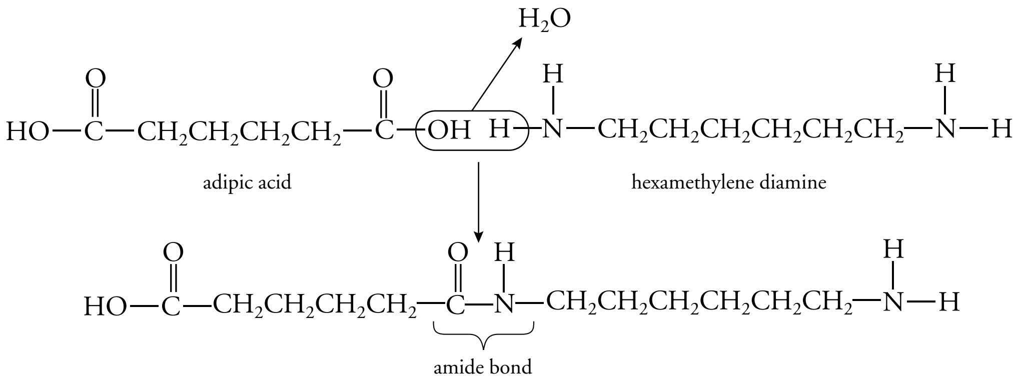
Condensation polymerization



$$\text{A—A—A—A—A—A—OH}\quad\text{H—B—B—B—B—B—B}\xrightarrow{-H_2O}\text{A—A—A—A—A—A—B—B—B—B—B—B}+H_2O$$

In this example, an OH group from one molecule combines with an H from another, forming a water molecule. At the same time, the two molecules A and B become joined by a covalent bond. If this can be made to happen at both ends of A and B, long chains are formed and a **condensation polymer** (also called a **step-growth polymer**) is the result.

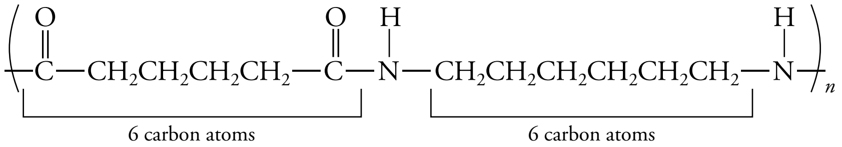
The two most familiar condensation polymers are nylon and polyesters. Nylon is formed by combining two different compounds, so it's considered a **copolymer**. The first nylon to be manufactured is called **nylon 6,6** because it forms by combining two compounds each with six carbon atoms.



Notice that adipic acid contains two carboxyl groups (it's called a dicarboxylic acid). The other compound is a diamine because it has two amine groups. By the elimination of water, the two molecules become joined by an *amide bond,* which we discussed in Section 23.4. This same linkage is found in proteins, including silk and the proteins found in our bodies.

■ As you will see later, the amide bond is found in polypeptides, the major component of proteins.

The reaction product with the amide bond still has a carboxyl group on one end and an amine group on the other, so further condensation can occur, ultimately leading to the formation of nylon 6,6.

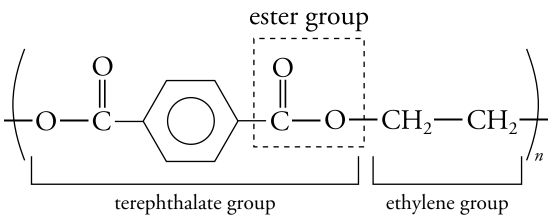


$$\left(\underbrace{\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}}_{\text{6 carbon atoms}}-\overset{H}{\overset{|}{N}}-\underbrace{CH_2CH_2CH_2CH_2CH_2CH_2}_{\text{6 carbon atoms}}-\overset{H}{\overset{|}{N}}\right)_n$$

Nylon 6,6

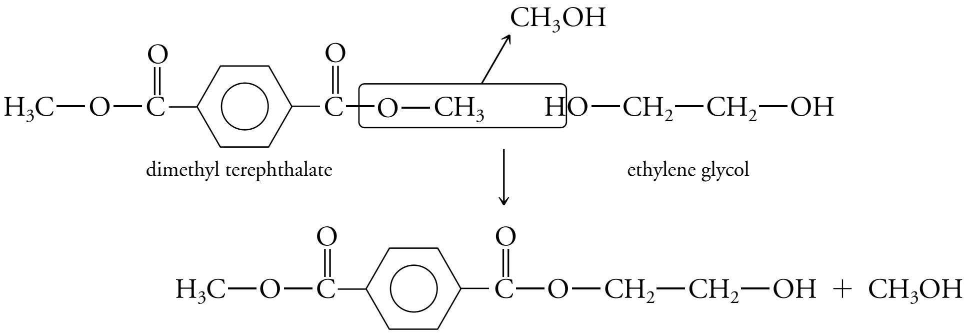
Nylon was invented in 1940 and became popular as a substitute for silk in women's stockings. It forms strong elastic fibers and is used to make fishing line as well as fibers found in all sorts of clothing and many other products.

Another type of condensation polymer uses the formation of an ester bond to join the monomers. An example of this is polyester, which is shown below.



poly(ethylene terephthalate), also known as PET

This copolymer is made by condensation of ethylene glycol, an alcohol, and dimethyl terephthalate, an ester. The first step is as follows:

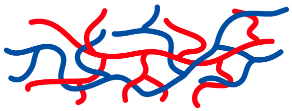


Notice that this time the small molecule that's displaced is CH_3OH, methyl alcohol, not H_2O. Continued polymerization ultimately leads to the PET polymer shown above. You may have heard of this polymer because it also goes by the name *Dacron*.

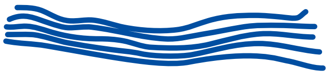
A variety of monomers can be used to form different polyesters with a range of properties. Their uses include fibers for fabrics, shatterproof plastic bottles for water and soft drinks, Mylar for making recording tapes and balloons that don't easily deflate, and shatterproof windows and eyeglasses.

Physical Properties and Polymer Crystallinity

Beyond chemical stability, physical properties are the features of polymers most sought after. Desirable properties of Teflon, for example, are its chemical inertness and its slipperiness toward just about anything. Nylon isn't eaten by moths—a chemical property, in fact—but its superior strength and its ability to be made into fibers and fabrics of great beauty are what make nylon valuable. Dacron (a polyester) resists mildewing and its fibers are not weakened by mildew like those of cotton. Dacron also has greater strength with lower mass than cotton, and Dacron fibers do not stretch as much, which are properties that account for Dacron's use for making sails.



(*a*) Two branched polymer chains become twisted with little order.



(*b*) Polymer chains are able to align, producing a tightly packed structure with a large degree of crystallinity.

Figure 23.4 | **Amorphous and crystalline polyethylene.** (*a*) When branching occurs in LDPE, the polymer strands are unable to become aligned and an amorphous product results. (*b*) Linear HDPE has a high degree of crystallinity, which makes for excellent strong fibers.

In many ways, the physical properties of a polymer are related to how the individual polymer strands are able to pack in the solid. For example, previously we noted that the least expensive way of making polyethylene yields a product that has branching. The branches prevent the molecules from lining up in an orderly fashion, so the molecules twist and intertwine to give an essentially amorphous solid (which means it lacks the kind of order found in crystalline solids). See Figure 23.4*a*. This amorphous product is called *low density polyethylene* (*LDPE*); the polymer molecules have a relatively low molecular mass and the solid has little structural strength. LDPE is the kind of polyethylene used to make the plastic bags grocery stores use to pack your purchases.

Following different methods, polyethylene can be made to form without branching and with molecular masses ranging from 200,000 to 500,000 u. This polymer is called *linear* polyethylene or *high density polyethylene, HDPE*. In HDPE, the polymer strands are able to line up alongside each other to produce a large degree of order (and therefore, crystallinity), as illustrated in Figure 23.4*b*. This enables the molecules to form fibers easily, and because the molecules are large and packed so well, the London forces between them are very strong. The result is a strong, tough fiber. DuPont's Tyvek®, for example, is made from thin, crystalline HDPE polyethylene fibers randomly oriented and pressed together into a material resembling paper. It is lightweight, strong, and resists water, tears, punctures, and abrasion. Federal Express has been using it for years for envelopes, and builders use it to wrap new construction to prevent water and air intrusion, thereby lowering heating and cooling costs. Tyvek is also used to make limited-use protective clothing for use in hazardous environments.

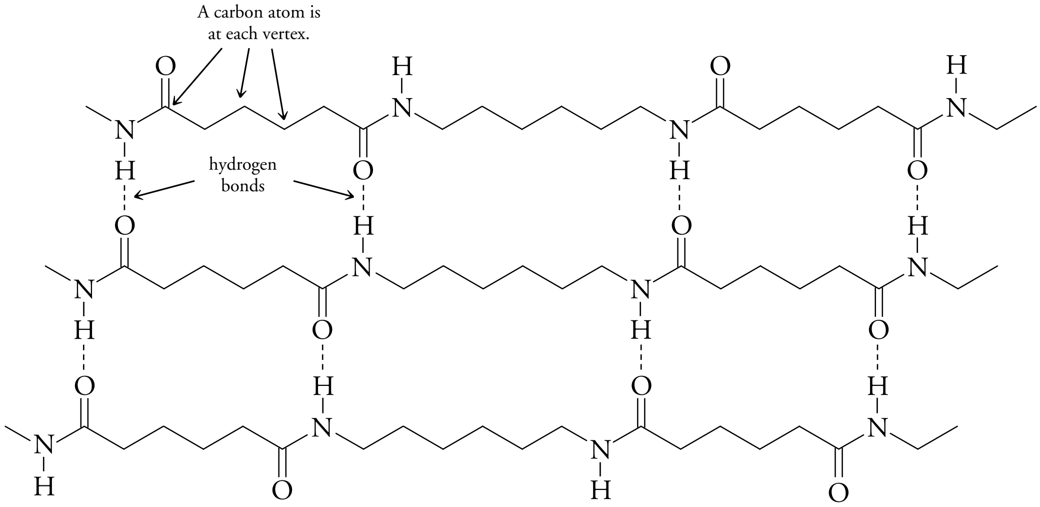
■ HDPE molecules contain approximately 30,000 CH_2 units linked end to end!

Under the right conditions, linear polyethylene molecules can be made extremely long, yielding *ultrahigh molecular weight polyethylene* (*UHMWPE*) with molecules having

■ UHMWPE molecules contain between 200,000 and 400,000 CH_2 units linked end to end!

molecular masses of three to six million. The fibers produced from this polymer are so strong that they are used to make bulletproof vests! Honeywell is producing an oriented polyethylene polymer it calls Spectra, which forms flexible fibers that can be woven into a strong, cut resistant fabric. It is used to make thin, lightweight liners for surgical gloves that resist cuts by scalpels, industrial work gloves, and even sails for sailboats (see Figure 23.5). Mixed with other plastics, it can be molded into strong rigid forms such as helmets for military or sporting applications.

Other good fiber-forming polymers also have long molecules with shapes that permit strong interactions between the individual polymer strands. Nylon, for example, possesses polar carbonyl groups, $\rangle C{=}O$, and N—H bonds that form strong hydrogen bonds between the individual molecules.



Three strands of nylon 6,6 bound to each other by hydrogen bonds.

Kevlar, another type of nylon, also forms strong hydrogen bonds between polymer molecules and is very crystalline. Its strong fibers are also used to make bulletproof vests. Because the fibers are so strong, they are also used to make thin yet strong hulls of racing boats. This lightweight construction improves speed and performance without sacrificing safety.

Figure 23.5 | **Spectra fibers.** Strong, lightweight sails made of Spectra fibers propelled Brad Van Liew to victory in the 2002–2003 "Around Alone" around-the-world yacht race. Van Liew sailed 31,094 miles in seven months to win the race. *(NewsCom)*

23.6 | Biochemical Compounds

Biochemistry is the systematic study of the chemicals of living systems, their organization into cells, and their chemical interactions. Biochemicals have no life in themselves as isolated compounds, yet life has a molecular basis. Only when chemicals are organized into cells in tissues can interactions occur that enable tissue repair, cell reproduction, the generation of energy, the removal of wastes, and the management of a number of other functions. The world of living things is composed mostly of organic compounds, including many natural polymers such as proteins, starch, cellulose, and the chemicals of genes.

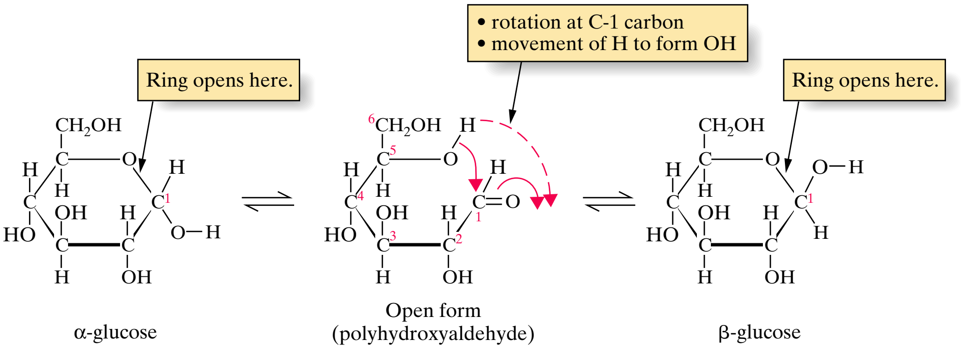
For its existence, a living system requires materials, energy, and information or "blueprints." Our focus in this section will be on the structures of substances that supply them—*carbohydrates, lipids, proteins,* and *nucleic acids*—the basic materials whose molecules, together with water and a few kinds of ions, make up cells and tissues.

■ Starch, table sugar, and cotton are all *carbohydrates.*

Carbohydrates

Most **carbohydrates,** which serve as a major source of the chemical energy we need to function, are polymers of simpler units called **monosaccharides.** The most common monosaccharide is glucose, a pentahydroxyaldehyde, and probably the most widely occurring structural unit in the entire living world. Glucose is the chief carbohydrate in blood, and

High-speed racing boats often are built with hulls made of Kevlar. Because of the polymer's high strength, the hulls can be made thin, thereby reducing weight and increasing speed. *(Martin Bond/ Photo Researchers)*



α-glucose

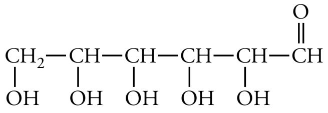
Open form
(polyhydroxyaldehyde)

β-glucose

Figure 23.6 | **Structures of glucose.** Three forms of glucose are in equilibrium in an aqueous solution. The curved arrows in the open form show how bonds become reoriented as it closes into a cyclic form. Depending on how the CH═O group is turned at the moment of ring closure, the new OH group at C-1 takes up one of two possible orientations, α or β. In these structures, the heavier bonds are used to indicate the part of the molecule that is closer to the viewer.

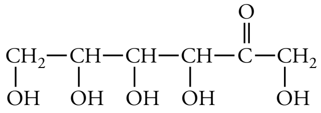
it provides the building unit for such important polysaccharides as cellulose and starch. Fructose, a pentahydroxyketone, is produced together with glucose when we digest table sugar. Honey is also rich in fructose.

When dissolved in water, the molecules of most monosaccharides exist in an equilibrium involving more than one structure. Glucose, for example, exists as two cyclic forms and one open-chain form in equilibrium in water (see Figure 23.6). The open-chain form, the only one with a free aldehyde group, is represented by less than 0.1% of the solute molecules. Yet, the solute in an aqueous glucose solution still gives the reactions of a polyhydroxyaldehyde. This is possible because the equilibrium between this form and the two cyclic forms shifts rapidly to supply more of any of its members when a specific reaction occurs to just one (in accordance with Le Châtelier's principle).



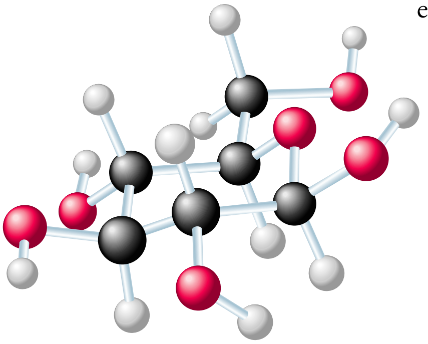
$$\underset{\text{OH}}{\text{CH}_2}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\overset{\text{O}}{\overset{\|}{\text{CH}}}$$

glucose (open-chain form)
a polyhydroxyaldehyde



$$\underset{\text{OH}}{\text{CH}_2}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\underset{\text{OH}}{\text{CH}_2}$$

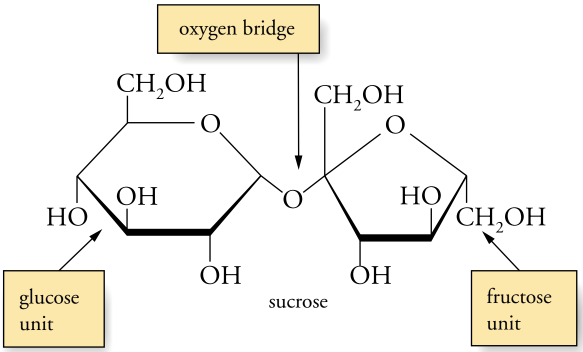
fructose (open-chain form)
a polyhydroxyketone



Because of the tetrahedral arrangement of atoms around each carbon, the six-membered rings of the cyclic forms of monosaccharides are not actually flat, as implied by the structural formulas we've drawn for them. The β-glucose molecule, for example, has the structure shown above.

Disaccharides

Carbohydrates whose molecules are split into two monosaccharide molecules by reacting with water are called **disaccharides.** *Sucrose* (table sugar, cane sugar, or beet sugar) is an example, and its hydrolysis gives glucose and fructose.



sucrose

To simplify, let's represent sucrose as Glu—O—Fru, where Glu is a glucose unit and Fru is a fructose unit, both joined by an oxygen bridge, —O—. The hydrolysis of sucrose, the chemical reaction by which we digest it, can thus be represented as follows.[3]

$$\underset{\text{sucrose}}{\text{Glu—O—Fru}} + H_2O \xrightarrow[\text{hydrolysis}]{\text{digestion}} \text{glucose} + \text{fructose}$$

Lactose (milk sugar) hydrolyzes to glucose and galactose (Gal), an isomer of glucose, and this is the reaction by which we digest lactose.

$$\underset{\text{lactose}}{\text{Gal—O—Glu}} + H_2O \xrightarrow[\text{hydrolysis}]{\text{digestion}} \text{galactose} + \text{glucose}$$

---

[3] Considerable detail is lost with the simplified structure of sucrose (and other carbohydrates like it to come). We leave the details, however, to other books because we seek a broader view.

Polysaccharides

Plants store glucose units for energy needs in molecules of **starch**, a type of large polymeric sugar molecule called a **polysaccharide**. Starch is found often in seeds and tubers (e.g., potatoes). It consists of two kinds of glucose polymers. The structurally simpler kind is *amylose*, which makes up roughly 20% of starch. We may represent its structure as follows, where O is the oxygen bridge linking glucose units.

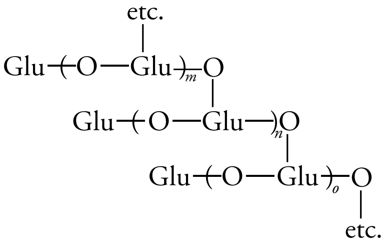
$$\text{Glu}-(\text{O}-\text{Glu})_n-\text{OH}$$

amylose; *n* is very large

The average amylose molecule has over 1000 glucose units linked together by oxygen bridges. These are the sites that are attacked and broken when water reacts with amylose during digestion. Molecules of glucose are released and are eventually delivered into circulation in the blood stream.

$$\text{Amylose} + n\text{H}_2\text{O} \xrightarrow[\text{(hydrolysis)}]{\text{digestion}} n \text{ glucose}$$

The bulk of starch is made up of *amylopectin*, whose molecules are even larger than those of amylose. The amylopectin molecule consists of several amylose molecules linked by oxygen bridges from the end of one amylose unit to a site somewhere along the "chain" of another amylose unit.



Amylopectin (*m*, *n*, and *o* are large numbers)

Molecular masses ranging from 50,000 to several million are observed for amylopectin samples from the starches of different plant species. (A molecular mass of 1 million corresponds to about 6000 glucose units.)

Animals store glucose units for energy as **glycogen,** a polysaccharide with a molecular structure very similar to that of amylopectin. When we eat starchy foods and deliver glucose molecules into the bloodstream, any excess glucose not needed to maintain a healthy concentration in the blood is removed from circulation by particular tissues, like the liver and muscles. Liver and muscle cells convert glucose to glycogen. Later, during periods of high energy demand or fasting, glucose units are released from the glycogen reserves so that the concentration of glucose in the blood stays high enough for the needs of the brain and other tissues.

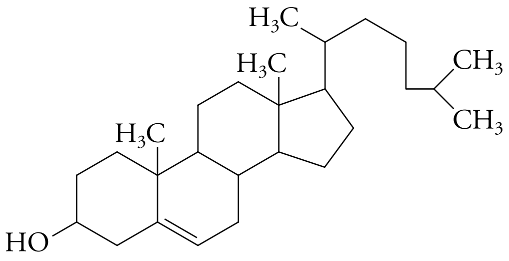
Cellulose

Cellulose is a polymer of glucose, much like amylose, but with the oxygen bridges oriented with different geometries. We lack the enzyme needed to hydrolyze its oxygen bridges, so we are unable to use cellulose materials like lettuce for food, only for fiber. Animals, such as cows that eat grass and leaves, have bacteria living in their digestive tracts that convert cellulose into small molecules, which the host organism then appropriates for its own use.

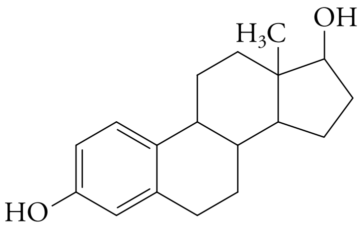
■ Cellulose is the chief material in a plant cell wall, and it makes up about 100% of cotton.

Lipids

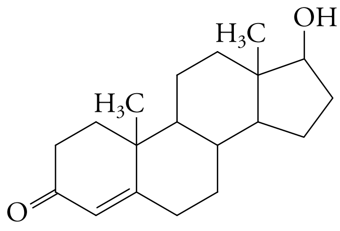
Lipids are natural products that are water insoluble, but tend to dissolve in nonpolar solvents such as diethyl ether or benzene. The lipid family is huge because the only structural requirement is that lipid molecules be relatively nonpolar with large segments that are entirely hydrocarbon-like. For example, the lipid family includes cholesterol as well as sex hormones, like estradiol and testosterone. You can see from their structures how largely hydrocarbon-like they are.



cholesterol



estradiol
(a female sex hormone)

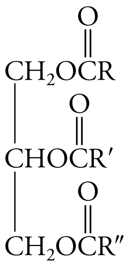


testosterone
(a male sex hormone)

Triacylglycerols

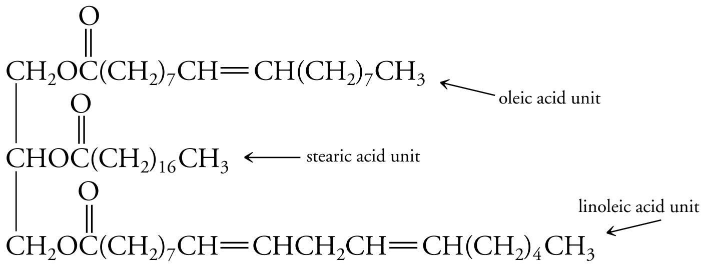
CH_2OH
|
$CHOH$
|
CH_2OH
glycerol

The lipid family also includes the edible fats and oils in our diets—substances such as olive oil, corn oil, butterfat, and lard. These are **triacylglycerols**, which are esters between glycerol, an alcohol with three OH groups, and any three of several long-chain carboxylic acids.



$$\begin{array}{l} \mathrm{CH_2O\overset{O}{\overset{\|}{C}}R} \\ | \\ \mathrm{CHO\overset{O}{\overset{\|}{C}}R'} \\ | \\ \mathrm{CH_2O\overset{O}{\overset{\|}{C}}R''} \end{array}$$

triacylglycerol
(general structural
features)



$$\begin{array}{l} \mathrm{CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3} \\ | \\ \mathrm{CHO\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3} \\ | \\ \mathrm{CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3} \end{array}$$

triacylglycerol—typical molecule present
in a vegetable oil

Cooking oils are advertised as *polyunsaturated* because of their several alkene groups per molecule.

The carboxylic acids used to make triacylglycerols are called **fatty acids** and generally have just one carboxyl group on an unbranched chain with an even number of carbon atoms (Table 23.4). Their long hydrocarbon chains make triacylglycerols mostly like hydrocarbons in physical properties, including insolubility in water. Many fatty acids have alkene groups.

Triacylglycerols obtained from vegetable sources, like olive oil, corn oil, and peanut oil, are called *vegetable oils* and are liquids at room temperature. Triacylglycerols from animal sources, like lard and tallow, are called *animal fats* and are solids at room temperature. The vegetable oils generally have more alkene double bonds per molecule than animal fats, and so are said to be *polyunsaturated*. The double bonds are usually cis, and so the molecules

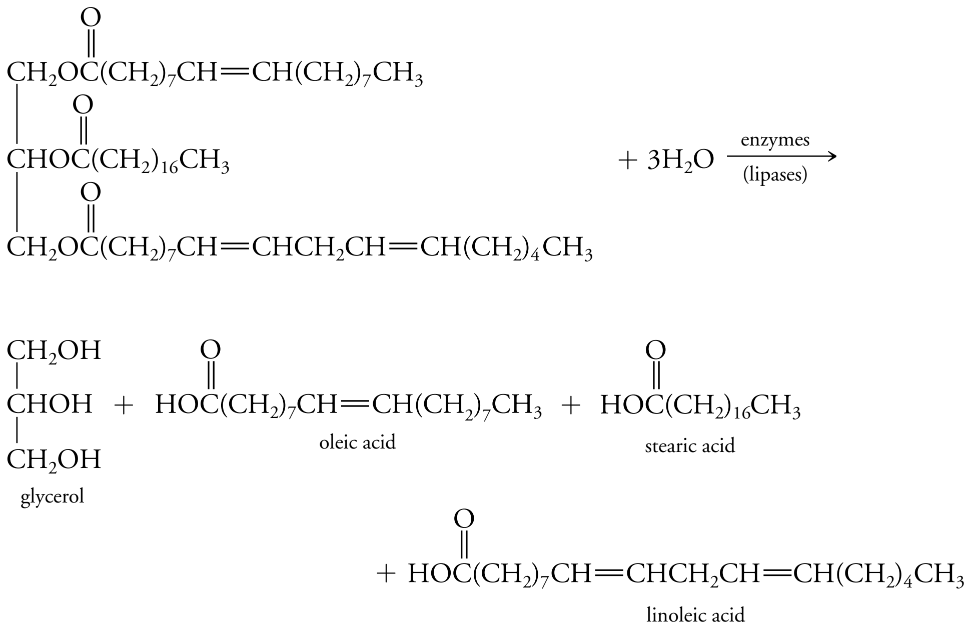
Table 23.4 Common Fatty Acids

Fatty Acid	Number of Carbon Atoms	Structure	Melting Point (°C)
Myristic acid	14	$CH_3(CH_2)_{12}CO_2H$	54
Palmitic acid	16	$CH_3(CH_2)_{14}CO_2H$	63
Stearic acid	18	$CH_3(CH_2)_{16}CO_2H$	70
Oleic acid	18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	4
Linoleic acid	18	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	−5
Linolenic acid	18	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	−11

are kinked, making it more difficult for them to nestle close together, experience London forces, and so be in the solid state.

Digestion of Triacylglycerols

We digest the triacylglycerols by hydrolysis, meaning by their reaction with water. Our digestive juices in the upper intestinal tract have enzymes called *lipases* that catalyze these reactions. For example, the complete digestion of the triacylglycerol shown previously occurs by the following reaction:



$$\begin{array}{l} CH_2O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CHO\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3 \\ | \\ CH_2O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \end{array} + 3H_2O \xrightarrow[\text{(lipases)}]{\text{enzymes}}$$

$$\underset{\text{glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{oleic acid}}{HO\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_7CH{=}CH(CH_2)_7CH_3} + \underset{\text{stearic acid}}{HO\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3}$$

$$+ \underset{\text{linoleic acid}}{HO\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3}$$

Actually, the *anions* of the acids form, because the medium in which lipid digestion occurs is basic.

When the hydrolysis of a triacylglycerol is carried out in the presence of sufficient base so as to release the fatty acids as their anions, the reaction is called *saponification*. A mixture of the salts of long-chain fatty acids is what makes up ordinary *soap*.

Hydrogenation of Vegetable Oils

Vegetable oils are generally less expensive to produce than butterfat, but because the oils are liquids, few people care to use them as bread spreads. Animal fats, like butterfat, are solids at room temperature, and vegetable oils differ from animal fats only in the number of carbon–carbon double bonds per molecule. Simply adding hydrogen to the double bonds of a vegetable oil, therefore, changes the lipid from a liquid to a solid.

Partial hydrogenation of a vegetable oil can lead to rearrangement of the atoms around the double bonds from cis to trans. The resulting products are known as *trans fats*. Because ingestion of trans fats has been associated with coronary artery disease, food product labels are now required to show the amounts of these fats in the food. Fast-food chains such as McDonalds, Wendy's, KFC, and Taco Bell have switched from using trans fat oils for cooking their French fries. In New York City, trans fats are banned from all restaurants.

■ Hydrogenation of a vegetable oil will add hydrogen atoms to both *cis* and *trans* isomers and result in a straight chain, saturated, molecule that maximizes the London attractive forces.

Cell Membranes in Animals

The lipids involved in the structures of cell membranes in animals are not triacylglycerols. Some are diacylglycerols with the third site on the glycerol unit taken up by an attachment to a phosphate unit. This, in turn, is joined to an amino alcohol unit by an ester-like network. The phosphate unit carries one negative charge, and the amino unit has a positive charge. These lipids are called *glycerophospholipids*. Lecithin is one example; it is used in cooking as an emulsifier.

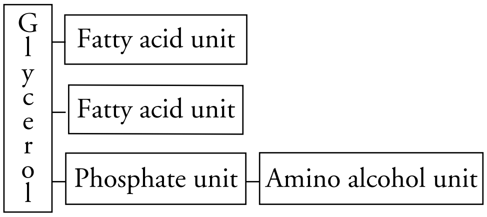
■ The amino alcohol unit in lecithin is contributed by choline, a cation:

$$HOCH_2CH_2\overset{+}{N}(CH_3)_3$$

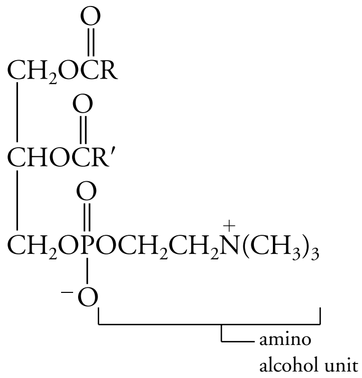
Ethanolamine (in its protonated form),

$$HOCH_2CH_2NH_3^+$$

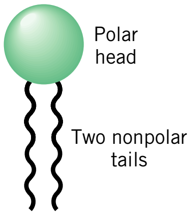
is another amino alcohol that occurs in phospholipids.


Glycerol
Fatty acid unit
Fatty acid unit
Phosphate unit
Amino alcohol unit

glycerophospholipid, general structure


$CH_2O\overset{O}{\overset{\|}{C}}R$
$CHO\overset{O}{\overset{\|}{C}}R'$
$CH_2O\overset{O}{\overset{\|}{P}}OCH_2CH_2\overset{+}{N}(CH_3)_3$
^-O
amino alcohol unit

a glycerophospholipid
(phosphatidylcholine, "lecithin")


Polar head
Two nonpolar tails

Glycerophospholipid symbol

The glycerophospholipids illustrate that it is possible for lipid molecules to carry polar, even ionic sites, and still not be very soluble in water. The combination of both nonpolar and polar or ionic units within the same molecule enable the glycerophospholipids and similar substances to be major building units for the membranes of animal cells.

The purely hydrocarbon-like portions of a glycerophospholipid molecule (the long R groups contributed by the fatty acid units) are **hydrophobic** ("water fearing;" they avoid water molecules). The portions bearing the electrical charges are **hydrophilic** ("water loving;" they are attracted to water molecules). In an aqueous medium, therefore, the molecules of a glycerophospholipid aggregate in a way that minimizes the exposure of the hydrophobic side chains to water and maximizes contact between the hydrophilic sites and water. These interactions are roughly what take place when glycerophospholipid molecules aggregate to form the *lipid bilayer* membrane of an animal cell (Figure 23.7). The hydrophobic side chains intermingle in the center of the layer where water molecules do not occur. The hydrophilic groups are exposed to the aqueous medium inside and outside of the cell. Not shown in Figure 23.7 are cholesterol and cholesterol ester molecules, which help to stiffen the membranes. Thus cholesterol is essential to the cell membranes of animals.

■ *Neurotransmitters* are small molecules that travel between the end of one nerve cell and the surface of the next to transmit the nerve impulse.

Cell membranes also include protein units, which provide several services. Some are molecular recognition sites for molecules such as hormones and neurotransmitters. Others provide channels for the movements of ions, like Na^+, K^+, Ca^{2+}, Cl^-, HCO_3^-, and others into or out of the cell. Some are channels for the transfer of small organic molecules, like glucose.

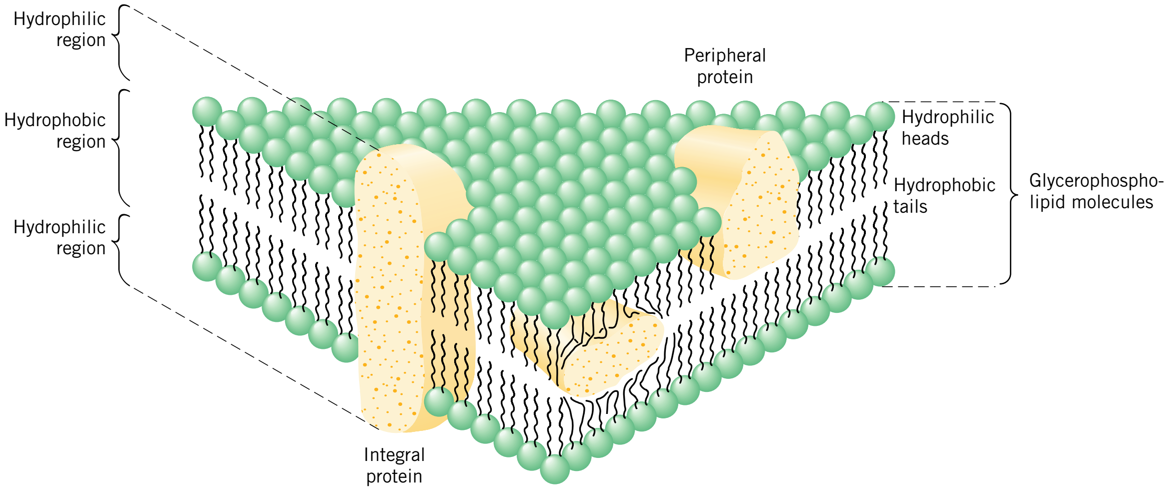

Hydrophilic region
Hydrophobic region
Hydrophilic region
Peripheral protein
Hydrophilic heads
Hydrophobic tails
Glycerophospholipid molecules
Integral protein

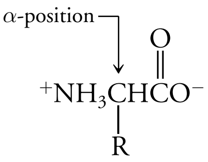
Figure 23.7 | **Animal cell membrane.** The lipid molecules of an animal cell membrane are organized as a bilayer.

Proteins

Proteins are a large family of substances that make up about half of the human body's dry weight. They are found in all cells and serve as enzymes, hormones, and neurotransmitters. They carry oxygen in the blood stream as well as some of the waste products of metabolism. No other group of compounds has such a variety of functions in living systems.

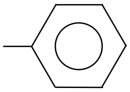
The dominant structural units of **proteins** are macromolecules called **polypeptides**, which are made from a set of monomers called **α-amino acids.** Most protein molecules include, besides their polypeptide units, small organic molecules or metal ions, and the whole protein lacks its characteristic biological function without these species.

The monomer units for polypeptides are a group of about 20 α-amino acids, all of which have structural features in common. Some examples of the set of 20 amino acids used to make proteins are given below. The symbol R stands for an *amino acid side chain.* All amino acids are known by their common names and each also has been given a three-letter symbol.



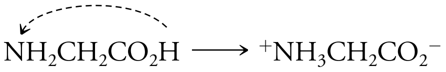
$${}^{+}NH_3\underset{R}{\underset{|}{\overset{\alpha\text{-position}\downarrow}{C}}}H\overset{O}{\overset{\|}{C}}O^-$$

α-amino acid, general structural features

R = H, glycine (Gly)
= CH_3, alanine (Ala)
= CH_2—  , phenylalanine (Phe)
= $CH_2CH_2CO_2H$, glutamic acid (Glu)
= $CH_2CH_2CH_2CH_2NH_2$, lysine (Lys)
= CH_2SH, cysteine (Cys)

The simplest amino acid is glycine, for which the "side chain" is H.

Glycine, like all of the amino acids in their pure states, exists as a *dipolar ion.* Such an ion results from an internal self-neutralization, by the transfer of a proton from the proton-donating carboxyl group to the proton-accepting amino group.



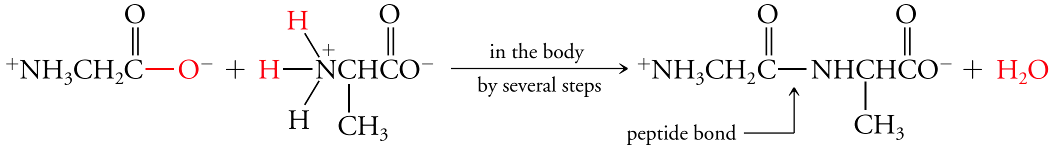
$$NH_2CH_2CO_2H \longrightarrow {}^{+}NH_3CH_2CO_2{}^-$$

glycine

glycine, dipolar ionic form

Polypeptides

Polypeptides are copolymers of the amino acids. The carboxyl group of one amino acid becomes joined to the amino group of another by means of an amide bond—the same kind of carbonyl–nitrogen bond found in nylon (page 1075), but here in a peptide it is called a **peptide bond.** Let's see how two amino acids, glycine and alanine, can become linked by a (multistep) splitting out of water.



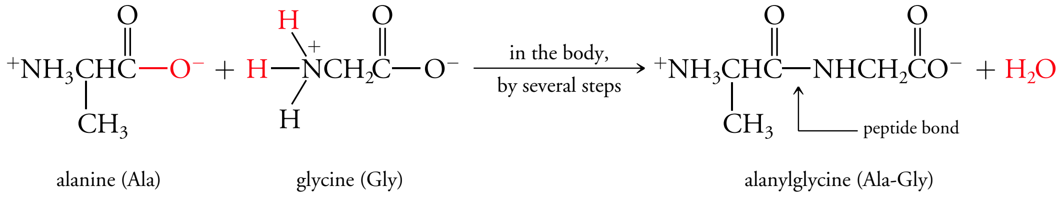
$${}^{+}NH_3CH_2\overset{O}{\overset{\|}{C}}—O^- + H—\underset{H}{\overset{H\ \ +}{N}}\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}O^- \xrightarrow[\text{by several steps}]{\text{in the body}} {}^{+}NH_3CH_2\overset{O}{\overset{\|}{C}}—NH\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}O^- + H_2O$$

peptide bond

glycine (Gly) alanine (Ala) glycylalanine (Gly-Ala)

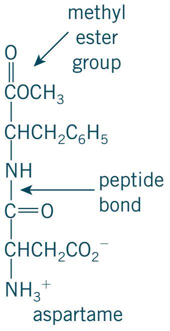
The product of this reaction, glycylalanine, is an example of a *dipeptide.* (Biochemists often use the three-letter symbols for the amino acids to describe the *structural* formulas of such products.)

We could have taken glycine and alanine in different roles and written the equation for the formation of a different dipeptide, Ala-Gly.



$$^{+}NH_3CH(CH_3)C(=O)-O^- + H-\overset{+}{N}H_2CH_2C(=O)-O^- \xrightarrow[\text{by several steps}]{\text{in the body,}} {}^{+}NH_3CH(CH_3)C(=O)-NHCH_2C(=O)O^- + H_2O$$

■ The artificial sweetener aspartame (NutraSweet®) is the methyl ester of a dipeptide.



The formation of these two dipeptides is like the formation of two 2-letter words from the letters N and O. Taken in one order we get NO; in the other, ON. They have entirely different meanings, yet are made of the same pieces.

Notice that each dipeptide, Gly-Ala and Ala-Gly, has a CO_2^- at one end of the chain and a $^+NH_3$ group at the other end. Each end of a dipeptide molecule, therefore, could form yet another peptide bond involving any of the 20 amino acids. For example, if glycylalanine were to combine with phenylalanine (Phe), two different *tripeptides* could form with the sequences Gly-Ala-Phe or Phe-Gly-Ala. Each of these tripeptides has a CO_2^- at one end and a $^+NH_3$ at the other end. Thus, you can see how very long sequences of amino acid units can be joined together.

As the length of a polypeptide chain grows, the number of possible combinations of amino acids becomes astronomical. For example, with just the three amino acids we've used (Gly, Ala, and Phe), six different polypeptide sequences are possible that differ only in the three side chains, H, CH_3, and $CH_2C_6H_5$ that are located at the α-carbon atoms.

Protein Structures

■ Hemoglobin is the oxygen carrier in blood.

Many proteins consist of a single polypeptide. Most proteins, however, involve assemblies of two or more polypeptides. These are identical in some proteins, but in others, the aggregating polypeptides are different. Moreover, a relatively small organic molecule may be included in the aggregation, and a metal ion is sometimes present, as well. Thus, the terms "protein" and "polypeptide" are not synonyms. Hemoglobin, for example, has all of the features just described (Figure 23.8). It is made of four polypeptides—two similar pairs—and four molecules of heme, the organic compound that causes the red color of blood. Heme, in turn, holds an iron(II) ion. The *entire* package is the protein, hemoglobin. If one piece is missing or altered in any way—for example, if iron occurs as Fe^{3+} instead of Fe^{2+}—the substance is not hemoglobin, and it does not transport oxygen in the blood.

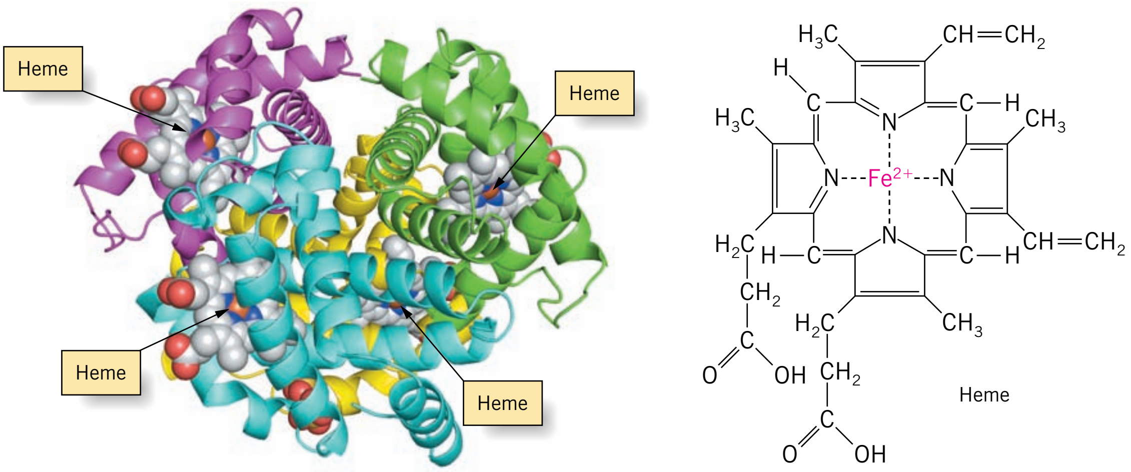


Figure 23.8 | **Hemoglobin.** Its four polypeptide chains, each shown as different colored ribbons, twist and bend around the four embedded heme units. Each heme unit contains an Fe^{2+} ion in its center that is able to bind to O_2.

Notice in Figure 23.8 how the strands of each polypeptide unit in hemoglobin are coiled and that the coils are kinked and twisted. Such shapes of polypeptides are determined by the amino acid sequence, because the side chains are of different sizes and some are hydrophilic and others are hydrophobic. Polypeptide molecules become twisted and coiled in whatever way minimizes the contact of hydrophobic groups with the surrounding water and maximizes the contacts of hydrophilic groups with water molecules. In addition, hydrogen bonding between N—H and C═O groups in neighboring loops help hold the shapes of the helices.

The final shape of a protein, called its *native form,* is as critical to its ability to function as anything else about its molecular architecture. For example, just the exchange of one side-chain R group by another changes the shape of hemoglobin and causes a debilitating condition known as sickle-cell anemia.

■ In one of the subunits of the hemoglobin in those with sickle-cell anemia, an isopropyl group, $—CH(CH_3)_2$, is a side-chain where a $—CH_2CH_2CO_2H$ side-chain should be.

Enzymes

The catalysts in living cells are called **enzymes**, and virtually all are proteins. Some enzymes require a metal ion, such as Mn^{2+}, Co^{2+}, Cu^{2+}, or Zn^{2+}, all of which are on the list of the *trace elements* that must be in a good diet. Some enzymes also require molecules of the B vitamins to be complete enzymes.

Some of our most dangerous poisons work by deactivating enzymes, often those needed for the transmission of nerve signals. For example, the botulinum toxin that causes botulism, a deadly form of food poisoning, deactivates an enzyme in the nervous system. Heavy metal ions, like Hg^{2+} or Pb^{2+}, are poisons because they also deactivate enzymes.

■ Heavy metal ions bond to the HS groups of cysteine side-chains in polypeptides.

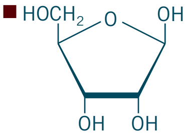
23.7 | Nucleic Acids

The polypeptides of an organism are made under the chemical direction of a family of compounds called the *nucleic acids*. Both the similarities and the uniqueness of every species as well as every individual member of a species depend on structural features of these compounds.

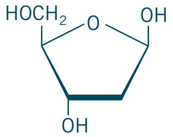
DNA and RNA

The **nucleic acids** occur as two broad types: **RNA**, or ribonucleic acids, and **DNA**, or deoxyribonucleic acids. DNA is the actual chemical of a gene and provides the chemical basis through which we inherit all of our characteristics.

The main chains or "backbones" of DNA molecules consist of alternating units contributed by phosphoric acid and a sugar molecule—a monosaccharide—as shown in Figure 23.9. In RNA, the monosaccharide is ribose (hence the R in RNA). In DNA, the monosaccharide is deoxyribose (*deoxy* means "lacking an oxygen unit"). Thus, both DNA

■ 

ribose



deoxyribose

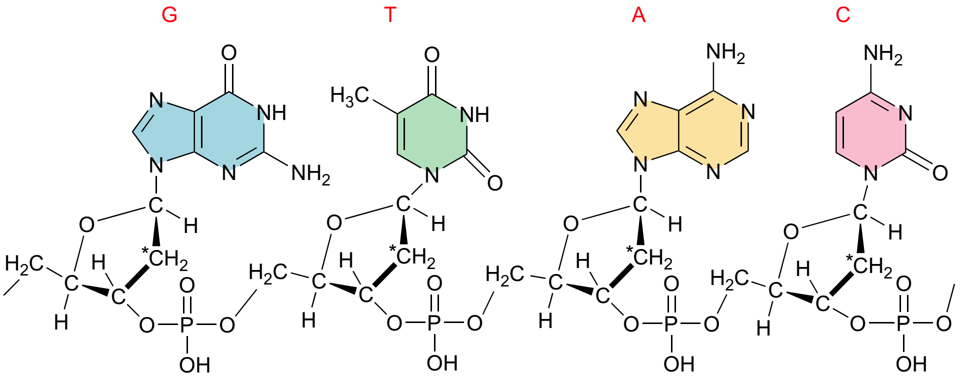
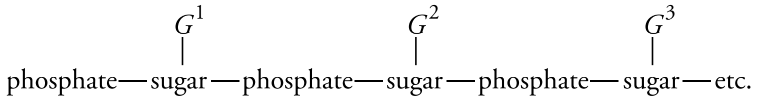


Figure 23.9 | **Nucleic acids.** A segment of a DNA chain featuring each of the four DNA bases. When the sites marked by asterisks each carry an OH group, the main "backbone" would be that of RNA. In RNA, U would replace T.

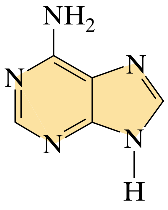
and RNA have the following systems, where *G* stands for *group* and each *G* unit represents a unique nucleic acid side chain.



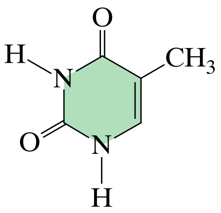
$$\begin{array}{ccccccccccc} & & G^1 & & & & G^2 & & & & G^3 \\ & & | & & & & | & & & & | \\ \text{phosphate} & — & \text{sugar} & — & \text{phosphate} & — & \text{sugar} & — & \text{phosphate} & — & \text{sugar}—\text{etc.} \end{array}$$

Backbone system in all nucleic acids is many thousands of repeating units long.
In DNA, the sugar is deoxyribose.
In RNA, the sugar is ribose.

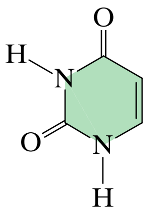
The side chains, *G*, are all heterocyclic amines whose molecular shapes have much to do with their function. Being amines, which are basic in water, they are referred to as the *bases* of the nucleic acids and are represented by single letters—A for adenine, T for thymine, U for uracil, G for guanine, and C for cytosine.



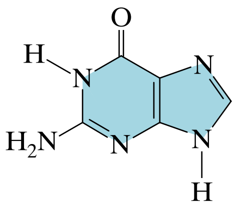
adenine
A



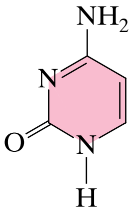
thymine
T



uracil
U



guanine
G



cytosine
C

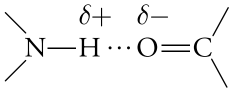
In DNA, the bases are A, T, G, and C; in RNA they are A, U, G, and C. These few bases are the "letters" of the genetic alphabet. Amazingly, the messages describing our entire genetic makeup are composed with just four "letters"—A, T, G, and C.

The DNA Double Helix

In 1953, F. H. C. Crick of England and J. D. Watson, an American, deduced that DNA occurs in cells as two intertwined, oppositely running strands of molecules coiled like a spiral staircase and called the **DNA double helix**. Hydrogen bonds help to hold the two strands side by side, but other factors are also involved.

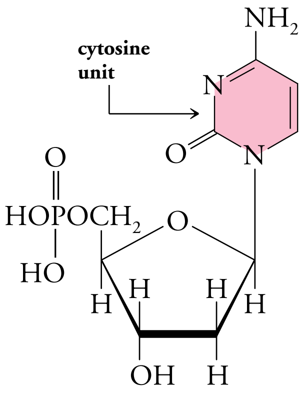
■ Crick and Watson shared the 1962 Nobel-Prize in Physiology or Medicine with Maurice Wilkins, using X-ray data from Rosalind Franklin to deduce the helical structure of DNA. The structure of DNA is illustrated in Figure 12.9 on page 534.

The bases have N—H and O═C groups, which enable hydrogen bonds (···) to form between them.



However, the bases with the best "matching" molecular geometries for maximum hydrogen bonding occur only as particular *pairs* of bases. The functional groups of each pair are in exactly the right locations in their molecules to allow hydrogen bonds between pair members. In DNA, A pairs only with T, never with G or C (see Figure 23.10). Similarly, C pairs only with G, never with A or T. Thus, opposite every G on one strand in a DNA double helix, a C occurs on the other. Opposite every A on one strand in DNA, a T is found on the other.

Adenine (A) can also pair with uracil (U), but U occurs in RNA. The A-to-U pairing is an important factor in the work of RNA.



a typical nucleotide, one using cytosine as its side chain

DNA Replication

Prior to cell division, the cell produces duplicate copies of its DNA so that each daughter cell will have a complete set. Such reproductive duplication is called DNA **replication**.

The accuracy of DNA replication results from the limitations of the base pairings: A only with T, and C only with G (Figure 23.11). The unattached letters, A, T, G, and C,

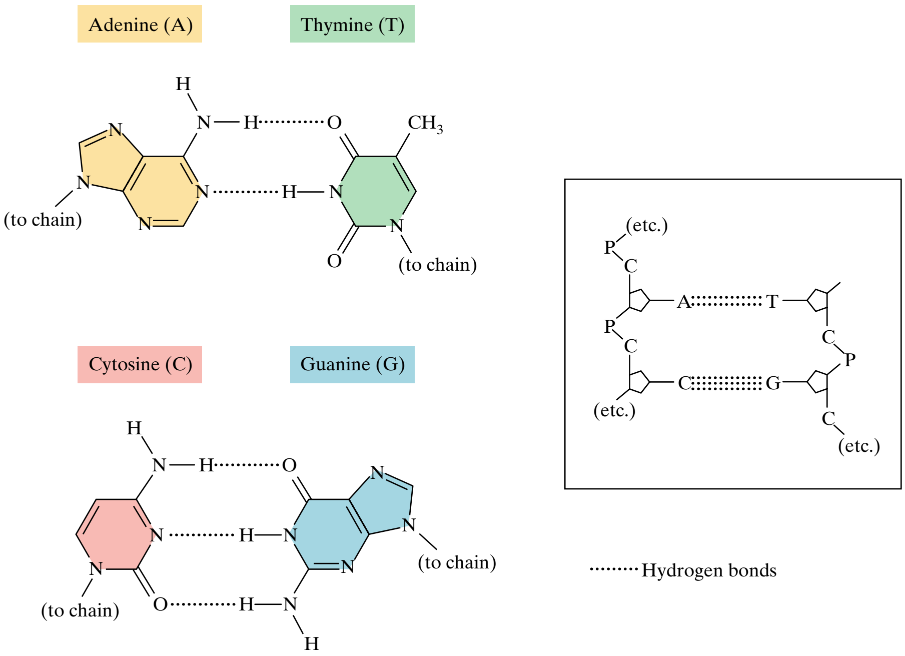

Adenine (A)
Thymine (T)
Cytosine (C)
Guanine (G)
(to chain)
(etc.)
Hydrogen bonds

Figure 23.10 | **Base pairing in DNA.** The hydrogen bonds are indicated by dotted lines.

in Figure 23.11 here represent not just the bases but the whole monomer molecules of DNA. The monomers are called *nucleotides* and are molecules made of a phosphate–sugar unit bonded to one particular base (see the illustration in the margin). The nucleotides are made by the cell and are present in the cellular "soup."

An enzyme catalyzes each step of replication. As replication occurs, the two strands of the parent DNA double helix separate, and the monomers for new strands assemble along the exposed single strands. Their order of assembling is completely determined by the specificity of base pairing. For example, a base such as T on a parent strand can accept only a nucleotide with the base A. Two daughter double helixes result that are identical to the parent, and each carries one strand from the parent. One new double helix goes to one daughter cell and the second goes to the other.

Genes and Polypeptide Synthesis

A single human gene has between 1000 and 3000 bases, but they do not occur continuously on a DNA molecule. In multicelled organisms, a gene is neither a whole DNA molecule nor a continuous sequence in one. A single gene consists of the totality of particular *segments* of a DNA chain that, taken together, carry the necessary genetic instruction for a particular polypeptide.

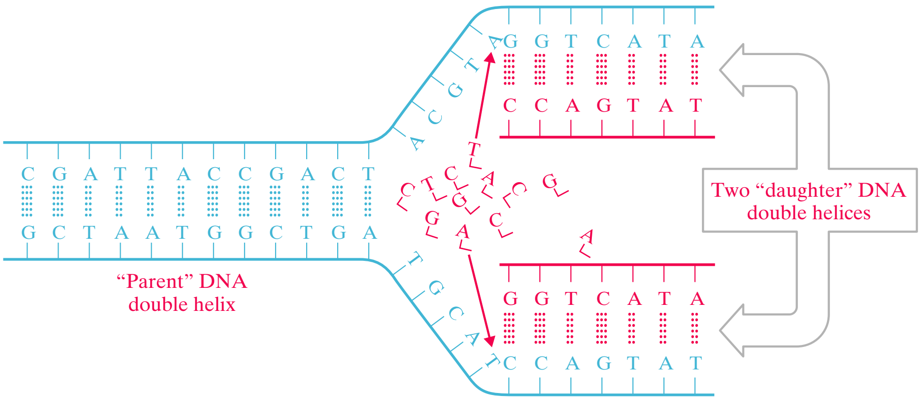

C G A T T A C C G A C T
G C T A A T G G C T G A
"Parent" DNA double helix
G G T C A T A
C C A G T A T
Two "daughter" DNA double helices

Figure 23.11 | **Base pairing and replication of DNA.**

Each polypeptide in a cell is made under the direction of its own gene. In broad outline, the steps between a gene and a polypeptide occur as follows.

$$\text{DNA} \xrightarrow{\text{transcription}} \text{RNA} \xrightarrow{\text{translation}} \text{Polypeptide}$$

gene	(The genetic message is read off in the cell nucleus and transferred to RNA.)	(The genetic message, now on RNA outside the nucleus, is used to direct the synthesis of a polypeptide.)

The step labeled **transcription** accomplishes just that—the genetic message, represented by a sequence of bases on DNA, is transcribed into a *complementary* sequence of bases on RNA, but U, not T, is on the RNA. **Translation** means the conversion of the base sequence on RNA into a side-chain sequence on a new polypeptide. It is like translating from one language (the DNA/RNA base sequences) to another language (the polypeptide side-chain sequence).

The translation step in polypeptide synthesis involves several steps and several different kinds of RNA. In the process, the cell tells which amino acid unit must come next in a growing polypeptide chain by means of a code that relates unique groups of three nucleic acid bases, called **codons**, to specific amino acids.

Which amino acid goes with which codon constitutes the **genetic code,** which enables the cell to translate from the four-letter RNA alphabet (A, U, G, and C) to the 20-letter alphabet of amino acids (the amino acid side chains). One of the most remarkable features of the code is that it is essentially universal. The codon specifying alanine in humans, for example, also specifies alanine in the genetic machinery of bacteria, aardvarks, camels, rabbits, and stinkbugs. Our chemical kinship with the entire living world is profound (even humbling).

Summary

Organic Compounds. **Organic chemistry** is the study of the covalent compounds of carbon, except for its oxides, carbonates, bicarbonates, and a few others. **Functional groups** attached to nonfunctional and hydrocarbon-like groups are the basis for the classification of organic compounds. Members of a family have the same kinds of chemical properties. Their physical properties are a function of the relative proportions of functional and nonfunctional groups. Opportunities for hydrogen bonding strongly influence the boiling points and water solubilities of compounds with OH or NH groups. Organic compounds exhibit isomerism because often there is more than one possible structure corresponding to a given molecular formula. Molecules containing an **asymmetric carbon atom** exhibit chirality.

Saturated Hydrocarbons. The **alkanes—saturated** compounds found chiefly in petroleum—are the least polar and the least reactive of the organic families. Their carbon skeletons can exist as **straight chains, branched chains,** or **rings.** When they are *open-chain*, there is free rotation about single bonds. Rings can include heteroatoms, but **heterocyclic compounds** are not hydrocarbons.

By the IUPAC rules, the names of alkanes end in *-ane*. A prefix denotes the carbon content of the parent chain, the longest continuous chain, which is numbered from whichever end is nearest a branch. The **alkyl groups** are alkanes minus a hydrogen.

Alkanes in general do not react with strong acids or bases. At high temperatures, their molecules crack to give H_2 and unsaturated compounds.

Unsaturated Hydrocarbons. The lack of free rotation at a carbon–carbon double bond makes **geometric isomerism** possible. The pair of electrons of a π bond makes alkenes act as Brønsted bases, enabling alkenes to undergo **addition reactions** with strong binary acids, or with water in the presence of an acid catalyst). Alkenes also add hydrogen (in the presence of a metal catalyst). Bromine and chlorine add to alkenes under mild, uncatalyzed conditions. Strong oxidizing agents, like ozone, readily attack alkenes and break their molecules apart.

Aromatic hydrocarbons, like benzene, do not give the addition reactions shown by alkenes. Instead, they undergo **substitution reactions** that leave the energy lowering, π electron network intact. In the presence of suitable catalysts, benzene undergoes these reactions with chlorine, bromine, nitric acid, and sulfuric acid.

Compounds Containing Oxygen. The **alcohols,** ROH, and the **ethers,** ROR′, are alkyl derivatives of water. Ethers have almost as few chemical properties as alkanes. Alcohols undergo an **elimination reaction** that splits out H_2O and changes them to alkenes. Concentrated strong binary acids, like HI, react with alcohols by a **substitution reaction,** which replaces the OH group by halogen. Oxidizing agents convert alcohols of the type RCH_2OH first into aldehydes and then into carboxylic acids. Oxidizing agents convert alcohols of the type R_2CHOH into ketones. Alcohols form esters with carboxylic acids.

Aldehydes, $RCH{=}O$, among the most easily oxidized organic compounds, are oxidized to carboxylic acids. **Ketones,**

RCOR′, strongly resist oxidation. Aldehydes and ketones add hydrogen to make alcohols.

The **carboxylic acids,** RCO_2H, are weak acids but neutralize strong bases. Their anions are Brønsted bases. Carboxylic acids can also be changed to esters by heating them with alcohols.

Esters, RCO_2R', react with water to give back their parent acids and alcohols. When aqueous base is used for hydrolysis, the process is called *saponification* and the products are the salts of the parent carboxylic acids as well as alcohols.

Derivatives of Ammonia. The simple **amines,** RNH_2, as well as their more substituted relatives, RNHR′ and RNR′R″, are organic derivatives of ammonia and thus are weak bases that can neutralize strong acids. The conjugate acids of amines are good proton donors and can neutralize strong bases.

The simple **amides,** $RCONH_2$, can be made from acids and ammonia, and they can be hydrolyzed back to their parent acids and trivalent nitrogen compounds. The amides are not basic.

Polymers. **Polymers,** which are **macromolecules,** are made up of a very large number of atoms in which a small characteristic feature repeats over and over many times. **Polypropylene,** a **chain-growth** or **addition polymer** that consists of a hydrocarbon **backbone** with a methyl group, CH_3, attached to every other carbon, is formed by **polymerization** of the **monomer** propylene. Polyethylene and polystyrene, which are also addition polymers, are formed from ethylene and styrene, respectively. **Condensation polymers (step-growth polymers)** are formed by elimination of a small molecule such as H_2O or CH_3OH from two monomer units accompanied by the formation of a covalent bond between the monomers. **Nylons** and **polyesters** are **copolymers** because they are formed from two different monomers.

The polymerization of ethylene can lead to **branching,** which produces an amorphous polymer called low-density polyethylene (LDPE). High-density polyethylene (HDPE) and ultrahigh-molecular-weight polyethylene (UHMWPE) are not branched and are more crystalline, which makes them stronger. Nylon's properties are affected by hydrogen bonding between polymer strands.

Carbohydrates. The glucose unit is present in starch, glycogen, cellulose, sucrose, lactose, and simply as a **monosaccharide** in honey. It's the chief "sugar" in blood. As a monosaccharide, glucose is a pentahydroxyaldehyde in one form but it also exists in two cyclic forms. The latter are joined by oxygen bridges in the **disaccharides** and **polysaccharides.** In lactose (milk sugar), a glucose and a galactose unit are joined. In sucrose (table sugar), glucose and fructose units are linked.

The major polysaccharides—starch (amylose and amylopectin), glycogen, and cellulose—are all polymers of glucose but with different patterns and geometries of branching. The digestion of the disaccharides and starch requires the hydrolyses of the oxygen bridges to give monosaccharides.

Lipids. Natural products in living systems that are relatively soluble in nonpolar solvents, but not in water, are members of a large group of compounds called **lipids.** They include sex hormones and cholesterol, the triacylglycerols of nutritional importance, and the glycerophospholipids and other phospholipids needed for cell membranes.

The **triacylglycerols** are triesters between glycerol and three of a number of long-chain, often unsaturated **fatty acids.** In the digestion of the triacylglycerols, the hydrolysis of the ester groups occurs, and anions of fatty acids form (together with glycerol).

Molecules of glycerophospholipids have large segments that are hydrophobic and others that are hydrophilic. Glycerophospholipid molecules are the major components of cell membranes, where they are arranged in a lipid bilayer.

Amino Acids, Polypeptides, and Proteins. The **amino acids** in nature are mostly compounds with NH_3^+ and CO_2^- groups joined to the same carbon atom (called the alpha position of the amino acid). About 20 amino acids are important to the structures of polypeptides and proteins.

When two amino acids are linked by a **peptide bond** (an amide bond), the compound is a dipeptide. In **polypeptides,** several (sometimes thousands) of regularly spaced peptide bonds occur, involving as many amino acid units. The uniqueness of a polypeptide lies in its chain length and in the sequence of the side-chain groups.

Some **proteins** consist of only one polypeptide, but most proteins involve two or more (sometimes different) polypeptides and often a nonpolypeptide (an organic molecule) and a metal ion.

Nearly all **enzymes** are proteins. Major poisons and some drugs work by deactivating enzymes.

Nucleic Acids. The formation of a polypeptide with the correct amino acid sequence needed for a given protein is under the control of **nucleic acids.** Nucleic acids are polymers whose backbones are made of a repeating sequence of pentose sugar units. On each sugar unit is a **base**—a heterocyclic amine such as adenine (A), thymine (T), guanine (G), cytosine (C), or uracil (U). In **DNA,** the sugar is deoxyribose, and the bases are A, T, G, and C. In **RNA,** the sugar is ribose and the bases are A, U, G, and C.

DNA exists in cell nuclei as **double helices.** The two strands are associated side by side, with hydrogen bonds occurring between particular pairs of bases. In DNA, A is always paired to T; C is always paired to G. The base U replaces T in RNA, and A can also pair with U. The bases, A, U, G, and C, are the four letters of the genetic alphabet, and the specific combination that codes for one amino acid in polypeptide synthesis are three bases, side by side, on a strand. The **replication** of DNA is the synthesis by the cell of exact copies of the original two strands of a DNA double helix.

Tools for Problem Solving

The following tools related to organic chemicals and their reactions were introduced in this chapter.

Condensed structures (page 1049)

The key to writing condensed structures is keeping in mind the number of covalent bonds formed by the nonmetals in achieving an octet.

Group 4A	4 bonds	Group 5A	3 bonds	Group 6A	2 bonds
Group 7A	1 bond	hydrogen	1 bond		

In writing a condensed structure, be sure the number of hydrogens with a given element is sufficient to make up the difference between the number of non-hydrogen atoms attached and the total number of bonds required by the element in question.

Polygons as condensed structures (page 1051)

A carbon atom is understood at each corner; other elements in the ring are explicitly written. Edges of the polygon represent covalent bonds; double bonds are explicitly shown. The remaining bonds, as required by the covalence of the atom at a corner, are understood to hold H atoms.

Functional groups (page 1052)

If you can recognize a functional group in a molecule, you can place the structure into an organic family and so predict the kinds of reactions the compound can give. In particular, study Table 23.1.

IUPAC rules of nomenclature for organic compounds

For alkanes (page 1054) The longest continuous chain of carbon atoms defines the parent chain for which the alkane is named. The chain is numbered from whichever end gives the lowest number to the first substituent. The name ending is *-ane*, and the prefixes that describe the number of carbon atoms in the chain are given on page 1054. The locations of alkyl substituents are specified by a number and a hyphen preceding the name of the alkyl group. Alkyl groups are specified in alphabetical order.

Alkenes and alkynes (page 1058) The name ending for alkenes is *-ene*, and the name ending for alkynes is *-yne*. The rules are similar to those for naming alkanes, except that the chain is numbered so that the first carbon of the double or triple bond has the lower of two possible numbers.

Alcohols (page 1061) The name ending for alcohols is *-ol*. The parent chain is the longest chain that includes the alcohol group and is numbered from whichever end gives the lowest number to the —OH group.

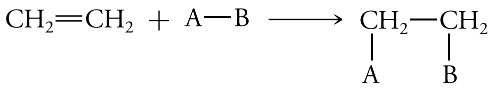
Aldehydes and ketones (page 1064) The name ending for aldehydes is *-al*. The parent chain is the longest chain that includes the aldehyde group. For ketones, the name ending is *-one*. The parent chain must include the carbonyl group and is numbered from whichever end gives the lowest number to the carbonyl carbon.

Carboxylic acids (page 1065) The name ending is *-oic acid*. The parent chain must include the carboxyl group.

Esters (page 1065) The name begins with the name of the alkyl group attached to the O atom. This is followed by a separate word taken from the name of the parent carboxylic acid, but altered by changing *-ic acid* to *-ate*.

Reactions of alkenes and alkynes (page 1059)

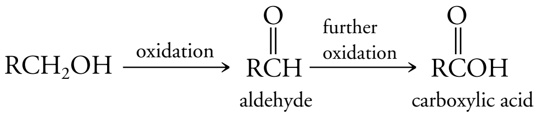
Components of a molecule add across a double bond.



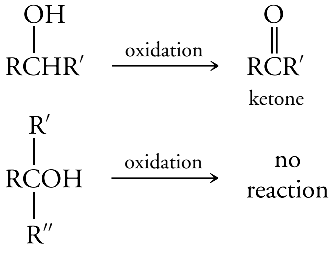
$$CH_2{=}CH_2 + A{-}B \longrightarrow \underset{\displaystyle A}{\underset{|}{CH_2}}{-}\underset{\displaystyle B}{\underset{|}{CH_2}}$$

Reactions of alcohols

Oxidation of alcohols (page 1061) The product(s) depend on the number of hydrogens attached to the alcohol carbon.



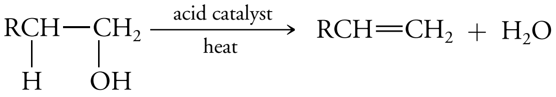
$$RCH_2OH \xrightarrow{\text{oxidation}} \underset{\text{aldehyde}}{R\overset{\overset{\displaystyle O}{\|}}{C}H} \xrightarrow[\text{oxidation}]{\text{further}} \underset{\text{carboxylic acid}}{R\overset{\overset{\displaystyle O}{\|}}{C}OH}$$



$$R\overset{\overset{OH}{|}}{C}HR' \xrightarrow{\text{oxidation}} \underset{\text{ketone}}{R\overset{\overset{O}{\|}}{C}R'}$$

$$R\overset{\overset{R'}{|}}{\underset{\underset{R''}{|}}{C}}OH \xrightarrow{\text{oxidation}} \text{no reaction}$$

Dehydration (page 1062)

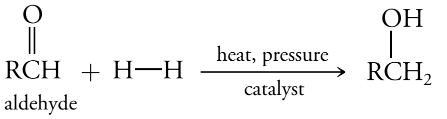


$$\underset{\underset{H}{|}}{RCH}-\underset{\underset{OH}{|}}{CH_2} \xrightarrow[\text{heat}]{\text{acid catalyst}} RCH{=}CH_2 + H_2O$$

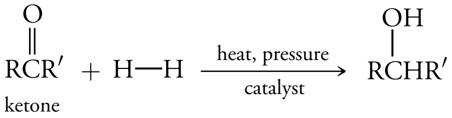
Substitution (page 1063)

$$ROH + HX\,(\text{conc.}) \xrightarrow{\text{heat}} RX + H_2O$$

Reactions of aldehydes and ketones: reduction (page 1064)



$$\underset{\text{aldehyde}}{R\overset{\overset{O}{\|}}{C}H} + H{-}H \xrightarrow[\text{catalyst}]{\text{heat, pressure}} R\overset{\overset{OH}{|}}{C}H_2$$



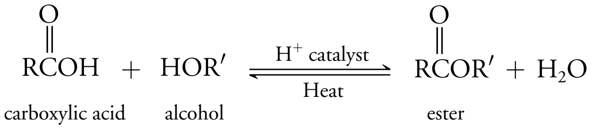
$$\underset{\text{ketone}}{R\overset{\overset{O}{\|}}{C}R'} + H{-}H \xrightarrow[\text{catalyst}]{\text{heat, pressure}} R\overset{\overset{OH}{|}}{C}HR'$$

Reactions of organic acids

Neutralization (page 1065) Carboxylic acids react with bases to give salts.

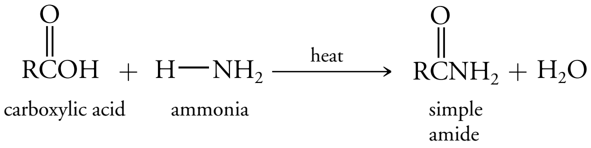
$$RCO_2H + OH^- \xrightarrow{H_2O} RCO_2^- + H_2O$$

Formation of esters (page 1066) Esters are formed in the reaction of a carboxylic acid with an alcohol.



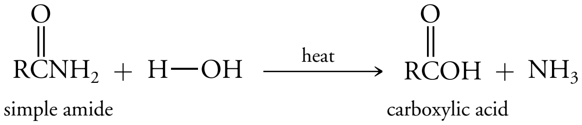
$$\underset{\text{carboxylic acid}}{R\overset{\overset{O}{\|}}{C}OH} + \underset{\text{alcohol}}{HOR'} \underset{\text{Heat}}{\overset{H^+ \text{ catalyst}}{\rightleftharpoons}} \underset{\text{ester}}{R\overset{\overset{O}{\|}}{C}OR'} + H_2O$$

Formation of amides (page 1069)



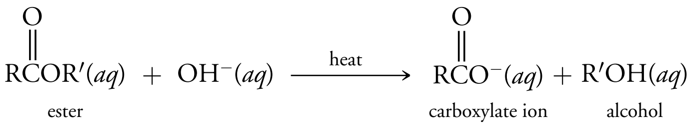
$$\underset{\text{carboxylic acid}}{R\overset{\overset{O}{\|}}{C}OH} + \underset{\text{ammonia}}{H{-}NH_2} \xrightarrow{\text{heat}} \underset{\text{simple amide}}{R\overset{\overset{O}{\|}}{C}NH_2} + H_2O$$

Hydrolysis of amides (page 1069)



$$\underset{\text{simple amide}}{R\overset{\overset{O}{\|}}{C}NH_2} + H{-}OH \xrightarrow{\text{heat}} \underset{\text{carboxylic acid}}{R\overset{\overset{O}{\|}}{C}OH} + NH_3$$

Saponification of esters (page 1066)



$$\underset{\text{ester}}{\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'}(aq)} + \mathrm{OH^-}(aq) \xrightarrow{\text{heat}} \underset{\text{carboxylate ion}}{\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O^-}(aq)} + \underset{\text{alcohol}}{\mathrm{R'OH}(aq)}$$

Addition polymerization (page 1072)

The addition of monomer units to a gradually growing chain by a free radical mechanism yields a long polymer chain. The repeating unit of the polymer has the formula of the monomer itself.

Condensation polymerization (page 1075)

Monomers are linked by the elimination of a small molecule such as H_2O or CH_3OH and the formation of a covalent bond between the remaining fragments. For copolymers, the repeating unit is that of the two monomers minus the small molecule that was eliminated.

PLUS = *WileyPLUS*, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the *WileyPLUS* system. **www.wileyplus.com.** **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk *.

Review Questions

Structural Formulas

23.1 In general terms, what makes possible so many organic compounds?

23.2 What is the condensed structure of R if R—CH_3 represents the compound ethane?

23.3 Which of the following structures are possible, given the numbers of bonds that various atoms normally form?

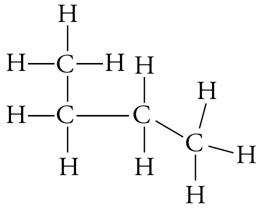
(a) $CH_2CH_2CH_3$

(b) $CH_3{=}CHCH_2CH_3$

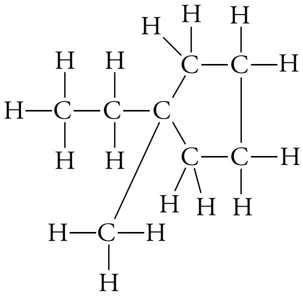
(c) $CH_3CH{=}CHCH_2CH_3$

23.4 Write condensed structures of the following:

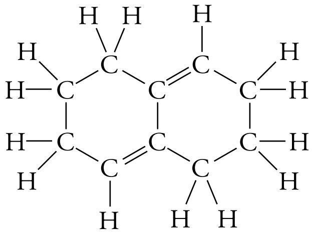
(a)



(b)



(c)

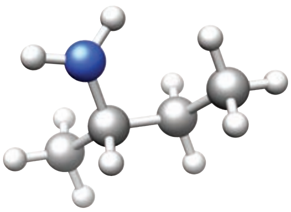


Families of Organic Compounds

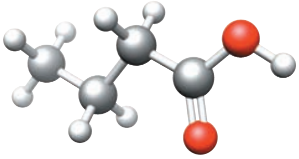
23.5 In $CH_3CH_2NH_2$, the NH_2 group is called the *functional* group. In *general terms*, why is it called this?

23.6 In general terms, why do functional groups impart more chemical reactivity to molecules that have them? Why don't the alkanes display as many reactions as, say, the amines?

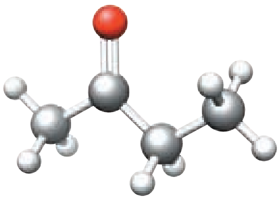
23.7 For each of the following, write the condensed structural formula and identify and name the functional group present in the molecule.



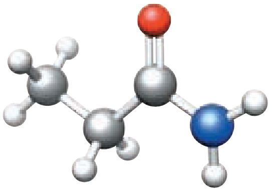
(a)



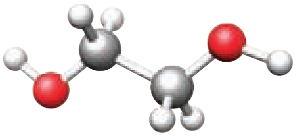
(b)



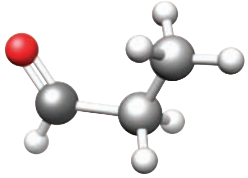
(c)



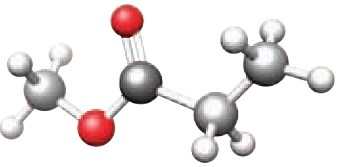
(d)



(e)



(f)



(g)

Isomers

23.8 What must be true about two substances if they are to be called isomers of each other?

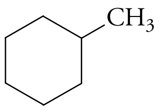
23.9 What prevents free rotation about a double bond and so makes geometric isomers possible?

Properties and Structure

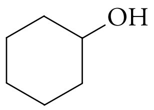
23.10 Explain why $CH_3CH_2CH_2OH$ is more soluble in water than $CH_3CH_2CH_2CH_3$.

23.11 Of the two compounds in Question 23.10, which has the higher boiling point? Explain.

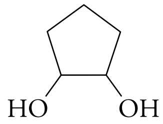
23.12 Examine the structures of the following compounds:



A



B

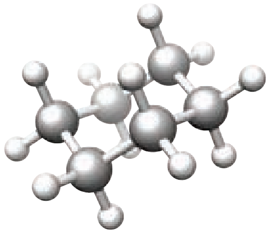


C

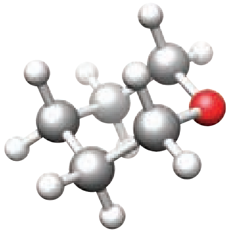
(a) Which has the highest boiling point? Explain.

(b) Which has the lowest boiling point? Explain.

23.13 Write condensed structures for the following. Which is more soluble in water? Explain.

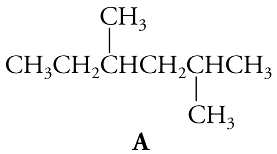


(a)



(b)

23.14 Which of the following compounds has the higher boiling point? Explain.



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{C}}HCH_3$$

A

$CH_3CH_2CH_2CH_2CH_3$

B

23.15 Why do aldehydes and ketones have boiling points that are lower than those of their corresponding alcohols?

23.16 Acetic acid boils at 118 °C, higher even than 1-propanol, which boils at 97 °C. How can the higher boiling point of acetic acid be explained?

23.17 Methyl ethanoate has many more atoms than its parent acid, ethanoic acid. Yet methyl ethanoate (BP 59 °C) boils at a much lower temperature than ethanoic acid (BP 118 °C). How can this be explained?

23.18 Ethanamide is a solid at room temperature. 1-Aminobutane, which has about the same molecular mass, is a liquid. Explain.

23.19 Amines, RNH_2, do not have boiling points as high as alcohols with comparable numbers of atoms. Why?

Names

23.20 Write the condensed structures of the following compounds:

(a) 2,2-dimethyloctane

(b) 1,3-dimethylcyclopentane

(c) 1,1-diethylcyclohexane

(d) 6-ethyl-5-isopropyl-7-methyloct-1-ene

(e) *cis*-pent-2-ene

23.21 Write condensed structures of the following compounds:

(a) 3-methylbutanal

(b) 4-methyloctan-2-one

(c) 2-chloropropanoic acid

(d) 1-methylethyl ethanoate

(e) 2-methylbutanamide

23.22 Write condensed structures of the following compounds:

(a) butan-2,3-dione

(b) butanedicarboxylic acid

(c) 2-aminopropanal

(d) cyclohexyl 2-methylpropanoate

(e) sodium 2,3-dimethylbutanoate

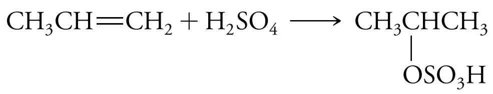
23.23 "3-Butanol" is not a proper name, but a structure could still be written for it. What is this structure, and what IUPAC name should be used?

23.24 No number is needed to identify the location of the double bond in $CH_3CH{=}CH_2$, propene. Why?

Chemical Properties of Organic Compounds

23.25 What are the products of the complete combustion of any hydrocarbon, assuming an abundant supply of oxygen?

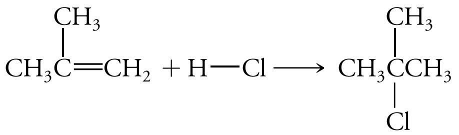
23.26 Propene is known to react with concentrated sulfuric acid as follows:



$$CH_3CH{=}CH_2 + H_2SO_4 \longrightarrow \underset{\substack{|\\ OSO_3H}}{CH_3CHCH_3}$$

The reaction occurs in two steps. Write the equation for the first step.

23.27 2-Methylpropene reacts with hydrogen chloride as follows:



$$CH_3\overset{\substack{CH_3\\ |}}{C}{=}CH_2 + H{-}Cl \longrightarrow CH_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Cl}}{C}}CH_3$$

The reaction occurs in two steps. Write the equation of each step.

23.28 The compound but-2-ene exists as two isomers, but when both isomers are hydrogenated, the products are identical. Explain.

23.29 Briefly explain how the C—O bond in isopropyl alcohol is weakened when a strong acid is present.

23.30 Which isomer of butanol cannot be oxidized by dichromate ion? Write its structure and IUPAC name.

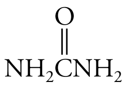
23.31 A monofunctional organic oxygen compound dissolves in aqueous base but not in aqueous acid. The compound is in which of the families of organic compounds that we studied? Explain.

23.32 A monofunctional organic nitrogen compound dissolves in aqueous hydrochloric acid but not in aqueous sodium hydroxide. What kind of organic compound is it?

23.33 Why are aqueous solutions of amides neutral while amines are basic?

***23.34** Hydrazine is a Brønsted base but urea does not exhibit basic properties. Offer an explanation.

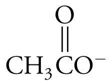
NH_2NH_2
hydrazine

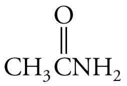
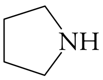


$NH_2\overset{\substack{O\\ \|}}{C}NH_2$
urea

23.35 Write the equilibrium that is present when $CH_3CH_2CH_2NH_2$ is in an aqueous solution.

23.36 Predict which of the following species can neutralize the hydronium ion in dilute, aqueous HCl at room temperature.

(a)  $CH_3\overset{\substack{O\\ \|}}{C}O^-$ **(c)** HO^- **(e)** $CH_3CH_2CH_2CH_3$

(b) CH_3NH_2 **(d)**  $CH_3\overset{\substack{O\\ \|}}{C}NH_2$ **(f)** 

23.37 Write the products that can be expected to form in the following situations. If no reaction occurs, write "no reaction."

(a) $CH_3CH_2CH_2NH_2 + HBr(aq) \longrightarrow$
(b) $CH_3CH_2CH_2CH_3 + HI(aq) \longrightarrow$
(c) $CH_3CH_2CH_2NH_3^+ + H_3O^+ \longrightarrow$
(d) $CH_3CH_2CH_2NH_3^+ + OH^- \longrightarrow$

23.38 Write the equation for the equilibrium that is present in a solution of propanoic acid and methanol with a trace of strong acid.

Polymers

23.39 What is a *macromolecule*? Name two naturally occurring macromolecular substances.

23.40 What is a *polymer*? Are all macromolecules polymers?

23.41 What is a *monomer*? Draw structures for the monomers used to make **(a)** polypropylene, **(b)** polytetrafluroethylene, and **(c)** polyvinyl chloride.

23.42 What do we mean by the term *polymer backbone*?

23.43 What is the repeating unit in polypropylene? Write the formula for the polypropylene polymer. Give three uses for polypropylene.

23.44 How do propylene and the repeating unit in polypropylene differ?

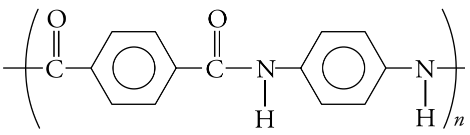
23.45 What is the difference between an *addition polymer* and *condensation polymer*?

23.46 Write the structure of polystyrene showing three of the repeating units. What are three uses for polystyrene plastic?

23.47 What is a *copolymer*?

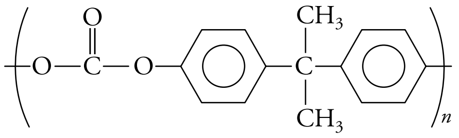
23.48 Write the structural formula for **(a)** nylon 6,6 and **(b)** poly(ethylene terephthalate).

23.49 The structural formula for Kevlar is



Identify the amide bond in this polymer.

23.50 Polycarbonate polymers are polyesters. An example is



Identify the structural feature that makes it a polyester. Identify the structural feature that makes it a poly*carbonate*.

23.51 What is meant by the term *branching* as applied to polymers? How does branching affect the properties of low-density polyethylene?

23.52 What is HDPE? Why does it form fibers easily?

23.53 What is UHMWPE? What range of molecular masses is found for this polymer?

23.54 How does polymer crystallinity affect the physical properties of the polymer?

23.55 Why doesn't low-density polyethylene form strong crystalline polymer fibers?

23.56 Why does nylon form strong fibers?

23.57 Show how hydrogen bonding can bind Kevlar polymer chains together. (See Question 23.49.)

23.58 What are some applications of crystalline polymers such as HDPE, UHMWPE, and Kevlar?

Biochemistry

23.59 What is biochemistry?

23.60 What are the three fundamental needs for sustaining life, and what are the general names for the substances that supply these needs?

Carbohydrates

23.61 How are carbohydrates defined?

23.62 What monosaccharide forms when the following polysaccharides are completely hydrolyzed? **(a)** starch, **(b)** glycogen, **(c)** cellulose

23.63 Glucose exists in three forms, only one of which is a polyhydroxyaldehyde. How, then, can an aqueous solution of any form of glucose undergo the reactions of an aldehyde?

23.64 Name the compounds that form when sucrose is digested.

23.65 The digestion of lactose gives what compounds? Name them.

23.66 The complete hydrolysis of the following compounds gives what product(s)? (Give the names only.)

(a) amylose **(b)** amylopectin

23.67 Describe the relationships among amylose, amylopectin, and starch.

23.68 Why are humans unable to use cellulose as a source of glucose?

23.69 What function is served by glycogen in the body?

Lipids

23.70 How are lipids defined?

23.71 Why are lipids more soluble than carbohydrates in nonpolar solvents?

23.72 Cholesterol is not an ester, yet it is defined as a lipid. Why?

23.73 A product such as corn oil is advertised as "polyunsaturated," but all nutritionally important lipids have unsaturated $C{=}O$ groups. What does "polyunsaturated" refer to?

23.74 Is it likely that the following compound could be obtained by the hydrolysis of a naturally occurring lipid? Explain.

$$CH_3(CH_2)_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$$

Amino Acids, Polypeptides, and Proteins

23.75 Describe the specific ways in which the monomers for all polypeptides are **(a)** alike and **(b)** different.

23.76 What is the peptide bond? How is it similar to the amide bond in nylon?

23.77 Describe the structural way in which two *isomeric* polypeptides would be different.

23.78 Describe the structural ways in which two different polypeptides can differ.

23.79 Why is a distinction made between the terms *polypeptide* and *protein*?

23.80 In general terms, what forces are at work that determine the final *shape* of a polypeptide strand?

23.81 What kind of substance makes up most enzymes?

23.82 The most lethal chemical poisons act on what kinds of substances? Give examples.

Nucleic Acids and Heredity

23.83 In general terms only, how does the body solve the problem of getting a particular amino acid sequence, rather than a mixture of randomly organized sequences, into a polypeptide?

23.84 In what specific structural way does DNA carry genetic messages?

23.85 What kind of force occurs between the two DNA strands in a double helix?

23.86 How are the two DNA strands in a double helix structurally related?

23.87 In what ways do DNA and RNA differ structurally?

23.88 Which base pairs with **(a)** A in DNA, **(b)** A in RNA, and **(c)** C in DNA or RNA?

23.89 The process of *transcription* begins with which nucleic acid and ends with which one?

23.90 The process of *translation* begins with which nucleic acid? What is the end result of translation?

Review Problems

Structural Formulas

23.91 Write full (expanded) structures for each of the following molecular formulas. Remember how many bonds the various kinds of atoms must have. In some you will have to use double or triple bonds. (*Hint:* A trial-and-error approach will have to be used.)

(a) CH_5N	**(c)** $CHCl_3$	**(e)** C_2H_2
(b) CH_2Br_2	**(d)** NH_3O	**(f)** N_2H_4

23.92 Write full (expanded) structures for each of the following molecular formulas. Follow the guidelines of Problem 23.91.

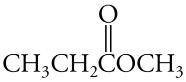
(a) C_2H_6	**(c)** CH_2O	**(e)** C_3H_3N
(b) CH_2O_2	**(d)** HCN	**(f)** CH_4O

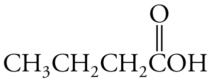
Families of Organic Compounds

23.93 Name the family to which each compound belongs.

(a) $CH_3CH{=}CH_2$

(b) CH_3CH_2OH

(c) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$

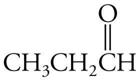
(d) 
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

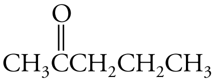
(e) $CH_3CH_2CH_2NH_2$

(f) $HOCH_2CH_2CH_3$

23.94 To what organic family does each compound belong?

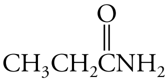
(a) $CH_3C{\equiv}CH$

(b) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(c) 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

(d) $CH_3{-}O{-}CH_2CH_3$

(e) $CH_3CH_2NH_2$

(f) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}NH_2$

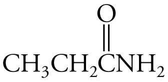
23.95 Identify by letter the compounds in Problem 23.93 that are saturated compounds.

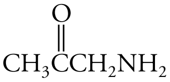
23.96 Which parts of Problem 23.94 give the structures of saturated compounds?

23.97 Classify the following compounds as amines or amides. If another functional group occurs, name it too.

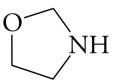
(a) $CH_3CH_2NH_2$

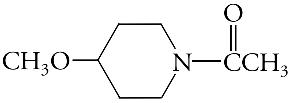
(b) $CH_3CH_2NHCH_3$

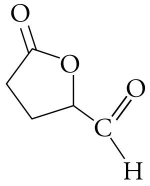
(c) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}NH_2$

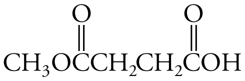
(d) 
$CH_3\overset{\overset{O}{\|}}{C}CH_2NH_2$

23.98 Name the functional groups present in each of the following structures:

(a) 

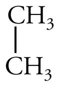
(b) 

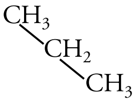
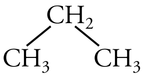
(c) 

(d) 
$CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

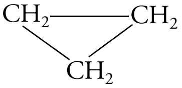
Isomers

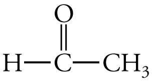
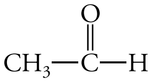
23.99 Decide whether the members of each pair are identical, are isomers, or are unrelated.

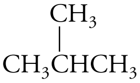
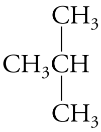
(a) $CH_3{-}CH_3$ and 
$\begin{array}{c}CH_3\\|\\CH_3\end{array}$

(b)  and 

(c) CH_3CH_2OH and $CH_3CH_2CH_2OH$

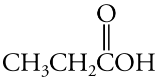
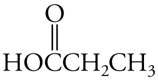
(d) $CH_3CH{=}CH_2$ and 

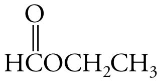
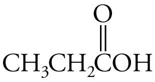
(e) 
$H{-}\overset{\overset{O}{\|}}{C}{-}CH_3$
and 
$CH_3{-}\overset{\overset{O}{\|}}{C}{-}H$

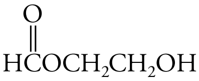
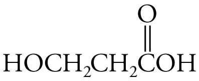
(f) 
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$
and 
$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H$

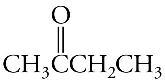
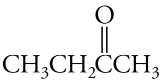
(g) $CH_3CH_2CH_2NH_2$ and $CH_3CH_2{-}NH{-}CH_3$

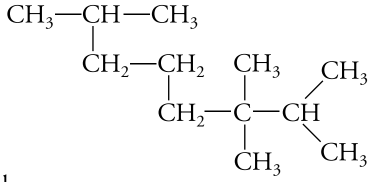
23.100 Examine each pair and decide if the two are identical, are isomers, or are unrelated.

(a) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}OH$
and 
$HO\overset{\overset{O}{\|}}{C}CH_2CH_3$

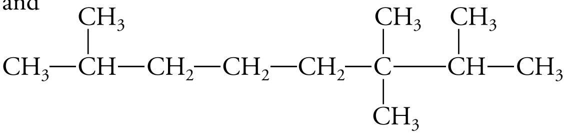
(b) 
$H\overset{\overset{O}{\|}}{C}OCH_2CH_3$
and 
$CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

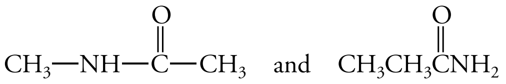
(c) 
$H\overset{\overset{O}{\|}}{C}OCH_2CH_2OH$
and 
$HOCH_2CH_2\overset{\overset{O}{\|}}{C}OH$

(d) 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$
and 
$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$

(e) 

and



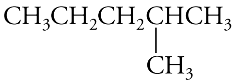
(f) 
$CH_3-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ and $CH_3CH_3\overset{\overset{\displaystyle O}{\|}}{C}NH_2$

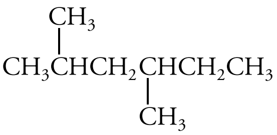
(g) $H-O-O-H$ and $H-O-H$

Names of Hydrocarbons

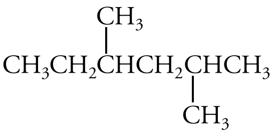
23.101 Write the IUPAC names of the following hydrocarbons:

(a) $CH_3CH_2CH_2CH_2CH_3$

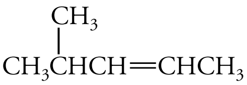
(b) 
$CH_3CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3$

(c) 
$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$

23.102 Write the IUPAC names of the following compounds:

(a) 
$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3$

(b) $CH_3CH_2CH{=}CHCH_2CH_3$

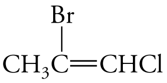
(c) 
$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH{=}CHCH_3$

Geometric Isomerism

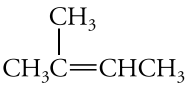
23.103 Write the structures of the cis and trans isomers, *if any,* for the following:

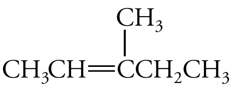
(a) $CH_2{=}CHBr$

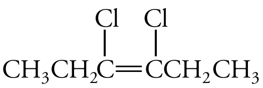
(b) $CH_3CH{=}CHCH_2CH_3$

(c) 
$CH_3\overset{\overset{\displaystyle Br}{|}}{C}{=}CHCl$

23.104 Write the structures of the cis and trans isomers, if any, for the following compounds:

(a) 
$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCH_3$

(b) 
$CH_3CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH_3$

(c) 
$CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{C}{=}\overset{\overset{\displaystyle Cl}{|}}{C}CH_2CH_3$

Chemical Reactions of Alkenes

23.105 Write the structures of the products that form when ethylene reacts with each of the following substances by an addition reaction. (Assume that needed catalysts or other conditions are provided.)

(a) H_2 **(c)** Br_2 **(e)** $HBr(g)$
(b) Cl_2 **(d)** $HCl(g)$ **(f)** H_2O (in acid)

23.106 The isopropyl cation is more stable than the propyl cation, so the former forms almost exclusively when propene undergoes addition reactions with proton-donating species. On the basis of this fact, predict the final products of the reaction of propene with each of the following reagents:

(a) hydrogen chloride

(b) hydrogen iodide

(c) water in the presence of an acid catalyst

23.107 Repeat Problem 23.105 using but-2-ene.

23.108 Repeat Problem 23.106 using cyclohexene.

23.109 In general terms, why doesn't benzene undergo the same kinds of addition reactions as cyclohexene?

23.110 If one mole of benzene were to *add* one mole of Br_2, what would form? What forms, instead, when Br_2, benzene, and an $FeBr_3$ catalyst are heated together? (Write the structures.)

Structures and Properties of Other Functional Groups

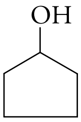
23.111 Write condensed structures and the IUPAC names for all of the saturated alcohols with three or fewer carbon atoms per molecule.

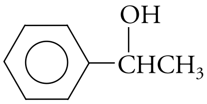
23.112 Write the condensed structures and the IUPAC names for all of the possible alcohols with the general formula $C_4H_{10}O$.

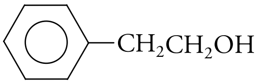
23.113 Write the condensed structures of all of the possible ethers with the general formula $C_4H_{10}O$. Following the pattern for the common names of ethers given in the chapter, what are the likely common names of these ethers?

23.114 Write the structures of the isomeric alcohols of the formula $C_4H_{10}O$ that could be oxidized to aldehydes. Write the structure of the isomer that could be oxidized to a ketone.

***23.115** Write the structures of the products of the acid-catalyzed dehydrations of the following compounds:

(a) 

(b) 

(c) 

23.116 Write the structures of the substitution products that form when the alcohols of Problem 23.115 are heated with concentrated hydroiodic acid.

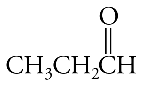
23.117 Write the structures of the aldehydes or ketones that can be prepared by the oxidation of the compounds given in Problem 23.115.

23.118 Write the structure of the product of the acid-catalyzed dehydration of propan-2-ol. Write the mechanism of the reaction.

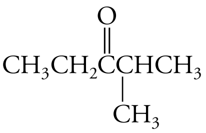
23.119 When ethanol is heated in the presence of an acid catalyst, ethene and water form; an elimination reaction occurs. When butan-2-ol is heated under similar conditions, *two* alkenes form (although not in equal quantities). Write the structures and IUPAC names of these two alkenes.

23.120 If the formation of the two alkenes in Problem 23.119 were determined purely by statistics, then the mole ratio of the two alkenes should be in the ratio of what whole numbers? Why?

23.121 Which of the following two compounds could be easily oxidized? Write the structure of the product of the oxidation.


$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

A

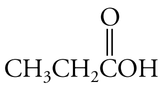

$CH_3CH_2\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{C}HCH_3$

B

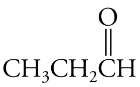
23.122 Which of the following compounds has the chemical property given below? Write the structure of the product of the reaction.

$CH_3CH_2CH_2OH$

A


$CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

B


$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

C

(a) Is easily oxidized

(b) Neutralizes NaOH

(c) Forms an ester with methyl alcohol

(d) Can be oxidized to an aldehyde

(e) Can be dehydrated to an alkene

23.123 Write the structures of the products that form in each of the following situations. If no reaction occurs, write "no reaction."

(a) $CH_3CH_2CO_2^- + HCl(aq) \longrightarrow$

(b) $CH_3CH_2CO_2CH_3 + H_2O \xrightarrow{\text{heat}}$

(c) $CH_3CH_2CH_2CO_2H + NaOH(aq) \longrightarrow$

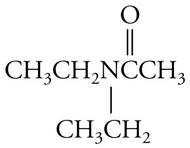
23.124 Write the structures of the products that form in each of the following situations. If no reaction occurs, write "no reaction."

(a) $CH_3CH_2CO_2H + NH_3 \xrightarrow{\text{heat}}$

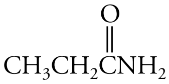
(b) $CH_3CH_2CH_2CONH_2 + H_2O \xrightarrow{\text{heat}}$

(c) $CH_3CH_2CO_2CH_3 + NaOH(aq) \xrightarrow{\text{heat}}$

***23.125** What organic products with smaller molecules form when the following compound is heated with water?


$CH_3CH_2\underset{\underset{CH_3CH_2}{|}}{N}\overset{\overset{O}{\|}}{C}CH_3$

23.126 Which of the following species undergo the reaction specified? Write the structures of the products that form.


$CH_3CH_2\overset{\overset{O}{\|}}{C}NH_2$

$CH_3CH_2CH_2NH_2$ $CH_3CH_2NH_3^+$

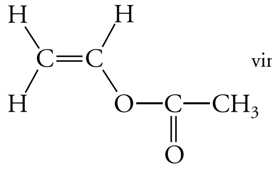
(a) Neutralizes dilute hydrochloric acid

(b) Hydrolysis

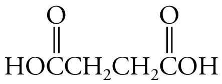
(c) Neutralizes dilute sodium hydroxide

Polymers

23.127 The structure of vinyl acetate is shown below. This compound forms a chain-growth polymer in the same way as ethylene and propylene. Draw a segment of the poly(vinyl acetate) polymer that contains three of the repeating units.

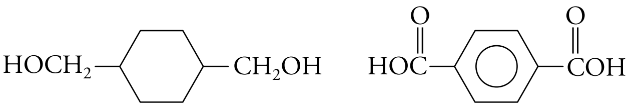

vinyl acetate

23.128 If the following two compounds polymerized in the same way that Dacron forms, what would be the repeating unit of their polymer?


$HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

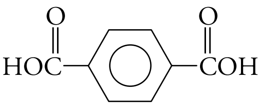
$HOCH_2CH_2OH$

23.129 Kodel, a polyester made from the following monomers, is used to make fibers for weaving crease-resistant fabrics.


monomers for Kodel

What is the structure of the repeating unit in Kodel?

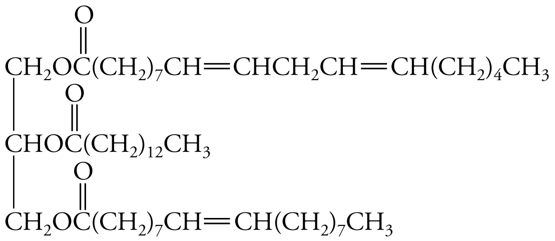
23.130 If the following two compounds polymerized in the same way that nylon forms, what would be the repeating unit in the polymer?


$NH_2CH_2CH_2CH_2CH_2NH_2$

Lipids

23.131 Write the structure of a triacylglycerol that could be made from palmitic acid, oleic acid, and linoleic acid.

23.132 Write the structures of the products of the complete hydrolysis of the following triacylglycerol:



$$\begin{array}{l} \mathrm{CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3} \\ | \\ \mathrm{CHO\overset{O}{\overset{\|}{C}}(CH_2)_{12}CH_3} \\ | \\ \mathrm{CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3} \end{array}$$

23.133 Write the structure of the triacylglycerol that would result from the complete hydrogenation of the lipid whose structure is given in Problem 23.132.

23.134 If the compound in Problem 23.132 is saponified, what are the products? Give their names and structures.

23.135 What parts of glycerophospholipid molecules provide hydrophobic sites? Which provide hydrophilic sites?

23.136 In general terms, describe the structure of the membrane of an animal cell. What kinds of molecules are present? How are they arranged? What forces keep the membrane intact? What functions are served by the protein components?

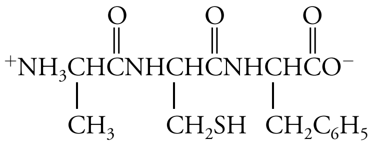
Amino Acids and Polypeptides

23.137 Write the structure of the dipeptide that could be hydrolyzed to give two molecules of glycine.

23.138 What is the structure of the tripeptide that could be hydrolyzed to give three molecules of alanine?

23.139 What are the structures of the two dipeptides that could be hydrolyzed to give glycine and phenylalanine?

23.140 Write the structures of the dipolar ionic forms of the amino acids that are produced by the complete digestion of the following compound:

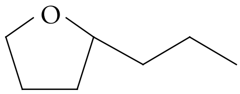


$$\mathrm{{}^{+}NH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}NH\underset{CH_2SH}{CH}\overset{O}{\overset{\|}{C}}NH\underset{CH_2C_6H_5}{CH}\overset{O}{\overset{\|}{C}}O^-}$$

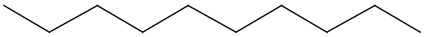
Additional Exercises

23.141 Write molecular formulas for the following:

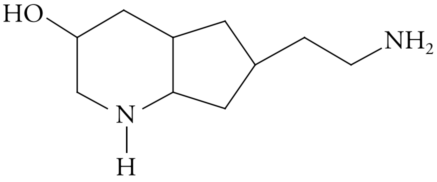
(a)



(b)



(c)



*23.142 The H_2SO_4-catalyzed addition of water to 2-methylpropene could give two isomeric alcohols.

(a) Write their condensed structures.

(b) Actually, only one forms. It is not possible to oxidize this alcohol to an aldehyde or to a ketone having four carbons. Which alcohol, therefore, is the product?

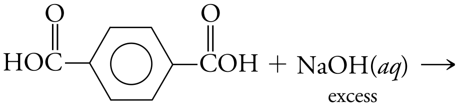
(c) Write the structures of the two possible carbocations that could form when sulfuric acid donates a proton to 2-methylpropene.

(d) One of the two carbocations of part (c) is more stable than the other. Which one is it, and how can you tell?

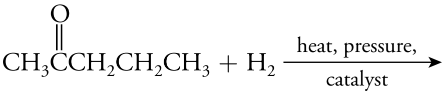
23.143 Suggest a reason why trimethylamine, $(CH_3)_3N$, has a *lower* boiling point (BP 3 °C) than dimethylamine, $(CH_3)_2NH$ (BP 8 °C), despite having a larger number of atoms.

23.144 Write the structures of the organic products that form in each situation. If no reaction occurs, write "no reaction."

(a)



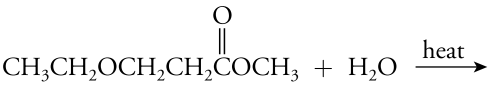
(b)



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + H_2 \xrightarrow[\text{catalyst}]{\text{heat, pressure,}}}$$

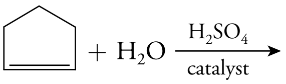
(c) $\mathrm{CH_3\overset{+}{N}H_2CH_2CH_2CH_3 + OH^-(\mathit{aq}) \longrightarrow}$

(d)

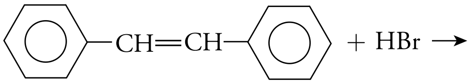


$$\mathrm{CH_3CH_2OCH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3 + H_2O \xrightarrow{\text{heat}}}$$

(e)



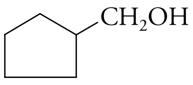
(f)



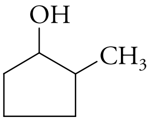
*23.145 How many tripeptides can be made from three different amino acids? If the three are glycine (Gly), alanine (Ala), and phenylalanine (Phe), what are the structures of the possible tripeptides. (*Hint:* Gly-Ala-Phe is one structure.)

Multi-Concept Problems

23.146 An unknown alcohol was either **A** or **B** below. When the unknown was oxidized with an *excess* of strong oxidizing agent, sodium dichromate in acid, the *organic* product isolated was able to neutralize sodium hydroxide.



A



B

(a) Which was the alcohol? Give the reasons for this choice.

(b) What is the molecular formula of the product of the oxidation?

(c) Draw the structural formula of the product.

(d) What is the minimum number of grams of sodium dichromate needed to oxidize 36.8 g of the alcohol?

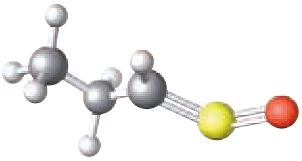
(e) If 36.8 g of the alcohol was oxidized and all of the product was collected, how many grams of NaOH could it neutralize?

23.147 Estimate the number of kilojoules of heat that would be liberated in the complete combustion of 11.35 g of gaseous compound B in the preceding problem. (*Hint:* Use bond energy data to estimate the standard heat of formation of the compound.)

23.148 A 6.225 mg sample of a monoprotic organic acid, when burned in pure oxygen, gave 12.44 mg of CO_2 and 5.091 mg H_2O. What are the empirical and molecular formulas for this acid? How many milliliters of 0.224 *M* KOH are needed to react completely with 0.822 g of the acid? Draw the structure of the ester that this acid would form with ethanol.

23.149 When 0.2081 g of an organic acid was dissolved in 50.00 mL of 0.1016 *M* NaOH, it took 23.78 mL of 0.1182 *M* HCl to neutralize the NaOH that was not used up by the sample of the organic acid. Calculate the formula mass from the data given. Is the answer necessarily the *molecular mass* of the organic acid? Explain.

23.150 The compound that causes your eyes to water when you chop an onion has the following molecular structure:



How many grams of oxygen would be required for the complete combustion of 1.225 g of this compound?

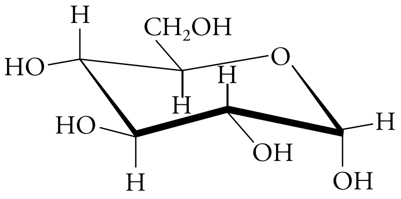
Exercises in Critical Thinking

23.151 The compound CH_2Cl_2 only exists as one isomer. Why does this support the statement that the H and Cl atoms in the compound are arranged tetrahedrally around the carbon rather than in a square planar structure?

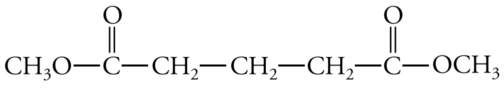
23.152 The α-carbon atom in an amino acid is a chiral center (except for glycine). Of the two possible enantiomers of these optically active substances, only one is produced naturally. What does this suggest about the mechanism whereby amino acids are synthesized in living creatures?

23.153 Use resonance structures to explain why urea, $(NH_2)_2C{=}O$, is not basic like typical amines. Without using resonance structures, use electronegativities to explain the same fact.

23.154 Below is the ring structure of a sugar molecule. How many chiral centers does this sugar molecule have? How many isomers are possible?



23.155 What would be the repeating unit of the polymer formed by condensation polymerization of the two monomers shown below?



$$CH_3O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

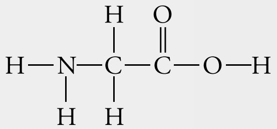
$$H_2N-CH_2-CH_2-NH_2$$

Chapters 21–23

Bringing It Together

Again we pause to provide you with an opportunity to see how well you have grasped concepts, how familiar you are with important terms, and how able you are at working chemistry problems. Keep in mind that many of the problems require tools developed in more than one chapter, including tools from Chapters 1–20. As you proceed, we encourage you to follow the approach taken by the worked examples you've studied.

1. Glycine, one of the important amino acids, has the structure



$$\mathrm{H{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O{-}H}$$

Calculate the atomization energy of this molecule from the data in Table 19.4.

2. Suppose that the total mass of the reactants in a chemical reaction is 100.00000 g. How many kilojoules of energy would have to evolve from this reaction if the total mass of the products will be 99.99900 g? If all this energy were used to heat water, how many liters of water could have its temperature raised from 10 °C to 100 °C?

3. Even though thorium does not undergo fission, it has been proposed as a fuel for nuclear reactors because it is abundant, can be easily converted to ^{233}U (an isotope that does undergo fission) by bombardment with low-energy neutrons, and because the production of nuclear weapons by this route is extremely difficult and hazardous. Formation of ^{233}U begins with the absorption of neutron by ^{232}Th. The product of that reaction then decays to ^{233}Pa, which then decays to ^{233}U. Write nuclear equations for the nuclear reactions described above. If fission of ^{233}U releases 197.9 MeV per atom, how many joules are released by fission of 100 g of ^{233}U?

4. How many gallons of octane, C_8H_{18}, having a density of 0.703 g cm^{-3}, would have to be burned to produce the same amount of energy as in the following production of 3.15 g of ^4_2He by the fusion reaction

$$^2_1H + {}^2_1H \longrightarrow {}^4_2He$$

Accurate atomic masses: $^2_1H = 2.014102$ u, $^4_2He = 4.002603$ u. For $C_8H_{18}(l)$, $\Delta H^\circ_f = 208.4$ kJ mol^{-1}.

5. Radium-226 (atomic mass = 226.03), the only naturally occurring isotope of this element, follows the decay sequence shown below.

$$^{226}Ra \xrightarrow[\text{1602 year}]{\alpha} {}^{222}Rn \xrightarrow[\text{3.82 day}]{\alpha} {}^{218}Po \xrightarrow[\text{3.10 min}]{\alpha} {}^{214}Pb$$

Each step occurs by alpha emission. The half-life for each step is shown below the arrow. How many years would it take for a 1.56 g sample of ^{226}Ra to produce 13.34 mL of helium measured at 27 °C and 674 torr following this decay sequence?

6. The reaction

$$Ni(H_2O)_6{}^{2+} + 6NH_3 \longrightarrow Ni(NH_3)_6{}^{2+} + 6H_2O$$

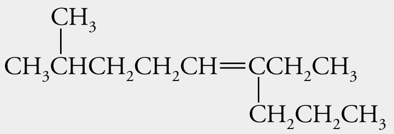
can be described as the displacement of one Lewis base by another. Explain. What is the Lewis acid in the reaction?

7. Sketch the chiral isomers of $[Cr(H_2O)_2(en)_2]^{3+}$. Is there a nonchiral isomer of this complex? What is the name of $[Cr(H_2O)_2(en)_2]Cl_3$?

8. When an aqueous solution of potassium tris(oxalato)cobaltate(III) is boiled, a redox reaction occurs in which some of the oxalate is oxidized to CO_2 and the cobalt(III) is reduced to cobalt(II), thereby destroying the complex. Suppose 0.556 g of the potassium tris(oxalato)cobaltate(III) is dissolved in water, boiled, and then the remaining oxalate is titrated in an acidic solution with 0.015 *M* $KMnO_4$ solution. During the titration, oxalate (actually present as oxalic acid in the acidified solution) is oxidized to CO_2 and the permanganate ion is reduced to manganese(II) ion. How many milliliters of the $KMnO_4$ solution will be required in the titration?

9. Which complex would absorb light of a shorter wavelength, $[V(H_2O)_6]^{3+}$ or $[V(CN)_6]^{3-}$? Justify your answer.

10. Name the following organic compound.



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH{=}\underset{\underset{CH_2CH_2CH_3}{|}}{C}CH_2CH_3$$

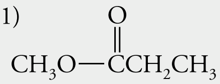
11. How many milliliters of H_2 measured at 766 torr and 25.6 °C are needed to hydrogenate the double bond in 12.4 g of the compound in the preceding question?

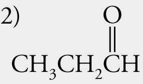
12. Draw the structure of 4-ethyl-2,2-dimethylheptan-3-ol. What is the name of the product that will form if this compound is oxidized with potassium dichromate in an acidic solution? Write a balanced equation for the combustion of this oxidation product in an excess supply of oxygen.

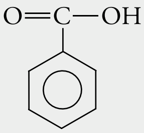
13. How many grams of $K_2Cr_2O_7$ are needed to oxidize 34.9 g of 4-ethyl-2,2-dimethylheptan-3-ol as described in the preceding problem?

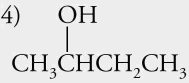
14. Proteins bind to metal ions using various amino acids. One such amino acid is cysteine, which has an S^- at the end of a carbon chain. Typically, four cysteine units use their sulfides to bind tightly to Zn(II) ions. The equilibrium dissociation constant for binding of Zn(II) at pH 7.0 is 8.0×10^{-12}. If the ΔH for the reaction is 26.8 kJ/mol, what is the value for ΔS for the reaction? What does this value for ΔS indicate about the entropy change for the reaction?

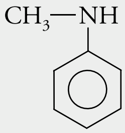
15. Which of the following compounds (a) neutralizes NaOH, (b) neutralizes HCl, (c) yields an alcohol and an organic acid when hydrolyzed, (d) is easily oxidized to an acid, (e) would be classified as aromatic, (f) would be oxidized to give a ketone?

(1)

$\mathrm{CH_3O{-}\overset{\overset{O}{\|}}{C}CH_2CH_3}$

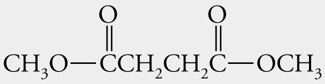
(2)

$\mathrm{CH_3CH_2\overset{\overset{O}{\|}}{C}H}$

(3)


(4)

$\mathrm{CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3}$

(5)


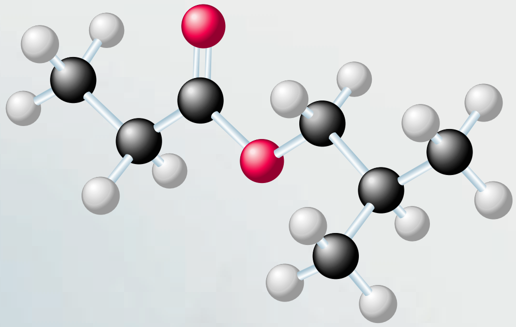
16. What would be the repeating structural unit if a condensation polymer were to form from the following monomers by the elimination of CH_3OH?


$\mathrm{CH_3O{-}\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}{-}OCH_3}$

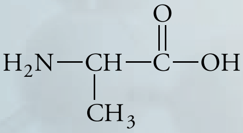
$\mathrm{H_2NCH_2CH_2CH_2NH_2}$

17. How do the water solubilities compare for monosaccharides and lipids? On the basis of their molecular structures, why do these differences exist?

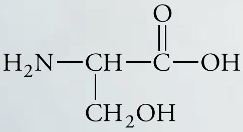
18. What are the names of the acid and alcohol from which the following ester is formed?



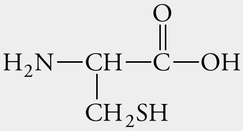
19. Write the structures of all of the tripeptides that could be made from the following if each tripeptide includes all three amino acids. If these amino acids could occur more than once, what is the total number of tripeptides they could form?


$\mathrm{H_2N{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}OH}$

Alanine
(Ala)


$\mathrm{H_2N{-}\underset{\underset{CH_2OH}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}OH}$

Serine
(Ser)


$\mathrm{H_2N{-}\underset{\underset{CH_2SH}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}OH}$

Cysteine
(Cys)

20. Sketch the structure of the $[FeF_6]^{4-}$ ion. How many unpaired electrons is it likely to have? Draw an energy level diagram showing the populations of the *d*-orbital energy levels in the complex. Write the mass action expression that corresponds to K_{form} for the complex.

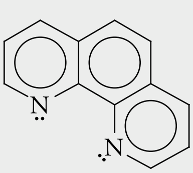
21. Deuterium, ^2_1H, can be incorporated into molecules in place of the common isotope, ^1_1H. Doing so can influence the rate of reaction. Would reaction rates be increased or decreased? Why?

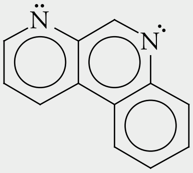
22. An organic compound was analyzed and found to contain 34.626% carbon and 3.874% hydrogen, the remainder being oxygen. A solution of the compound in water tested acidic, and when 0.463 g of the compound was dissolved in water, it required 26.56 mL of 0.3350 *M* NaOH for complete neutralization in a titration. What is the likely structural formula of the compound?

23. Strontium-90, a beta emitter, has a half-life of 28.1 yr. If 36.2 mg of ^{90}Sr were incorporated in the bones of a growing child, how many beta particles would the child absorb from this source in 1.00 day?

24. When uranium-238 is bombarded by a particular bombarding particle, it can be transmuted into plutonium-239 and neutrons. Which bombarding particle accomplishes this? How many neutrons are produced for each plutonium-239 atom? Write the nuclear equation for this change.

25. Which of the compounds below would most likely behave as a bidentate ligand? Explain your choice and why you eliminated the other two.


(a)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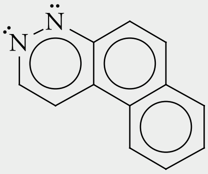
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Appendix A

Review of Mathematics

The purpose of this Appendix is to provide a brief review of math topics you will use in solving various chemistry problems in this book. We recommend that you refer to the topics discussed here when you find you are having difficulty in following the math in worked examples, when you are unsure as to how to proceed with solving the math in an exercise or homework problem, or when answers you obtain do not match those in Appendix B.

A.1 | Exponential and Scientific Notation

Very large and very small numbers are generally expressed as powers of ten. This is often called **exponential notation.** When the quantity is expressed as *a number between 1 and 10* multiplied by 10 raised to a power (e.g., 3.2×10^5), we also call it **standard scientific notation** (or simply **scientific notation**). Some examples are given in Table A.1. If you have a scientific calculator, it is able to express numbers in scientific notation and it permits you to perform arithmetic on numbers expressed this way. Some tips on using scientific calculators are described later in Appendix A.5.

Even though you have a calculator at your disposal, it is important that you understand how to write these numbers and how to perform arithmetic with them. Such an ability provides a way to quickly check an answer to a problem to be sure you've used the calculator correctly.

Table A.1

Number	Exponential Form
1	1×10^0
10	1×10^1
100	1×10^2
1000	1×10^3
10,000	1×10^4
100,000	1×10^5
1,000,000	1×10^6
0.1	1×10^{-1}
0.01	1×10^{-2}
0.001	1×10^{-3}
0.000 1	1×10^{-4}
0.000 01	1×10^{-5}
0.000 001	1×10^{-6}
0.000 000 1	1×10^{-7}

The Meaning of Positive and Negative Exponents

Positive Exponents

Suppose you come across a number such as 6.4×10^4. This is just an alternative way of writing 64,000. In other words, the number 6.4 is multiplied by 10 four times.

$$6.4 \times 10^4 = 6.4 \times 10 \times 10 \times 10 \times 10 = 64{,}000$$

Instead of actually writing out all of these 10s, notice that the decimal point is simply moved four places to the right in going from 6.4×10^4 to 64,000. Here are a few other examples. Study them to see how the decimal point changes.

$$53.476 \times 10^2 = 5347.6$$
$$0.0016 \times 10^5 = 160$$
$$0.000056 \times 10^3 = 0.056$$

Here is another example that more forcefully shows the value of expressing a number in scientific notation.

$$\begin{aligned}&602{,}000{,}000{,}000{,}000{,}000{,}000{,}000\\ &\quad = 6.02 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times\\ &\qquad\quad 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10\\ &\quad = 6.02 \times 10^{23}\end{aligned}$$

(This is Avogadro's number, which is the number of atoms in 12.0 g of carbon.)

In some calculations it is helpful to rewrite large numbers in scientific notation format. To do this, count the number of places you would have to move the decimal point to the left to put it just after the first digit in the number. For example, you would have to move the decimal point four places to the left in the following number.

$$6\;\underset{\underset{4}{\curvearrowleft}}{0}\;\underset{\underset{3}{\curvearrowleft}}{5}\;\underset{\underset{2}{\curvearrowleft}}{3}\;\underset{\underset{1}{\curvearrowleft}}{0}$$

Therefore, we can rewrite 60530 as 6.0530×10^4. Thus the number of moves equals the exponent.

Sometimes it is necessary to change a number from one exponential form to another. For example, suppose we wish to re-express the number 6.0530×10^4 as something times 10^2.

$$6.0530 \times 10^4 = \boxed{} \times 10^2$$

What number goes in the box? Although there are rules that you could learn, it is better to think it through as follows. The number 6.0530×10^4 is a product of two parts, 6.0530 and 10^4. Together they equal 60530. We want to change the exponential part to 10^2, which means the exponential part of the product is becoming *smaller*. The only way the product can remain equal to 60530 is if the decimal part becomes *larger*. Since we are decreasing the exponential part by a factor of 100 (i.e., 10^2), we must increase the decimal part by a factor of 100, which means we change it from 6.0530 to 605.30. Therefore,

$$6.0530 \times 10^4 = \boxed{605.30} \times 10^2$$

Negative Exponents

A negative exponent tells us to take the reciprocal of the quantity and raise it to the power expressed in the exponent. Thus, x^{-1} means $1/x$, and x^{-5} means $1/x^5$.

$$x^{-1} = \frac{1}{x} \qquad x^{-5} = \frac{1}{x^5}$$

Now, imagine you have just encountered a number such as 1.4×10^{-4}. This is an alternative way of writing

$$\frac{1.4}{10 \times 10 \times 10 \times 10}$$

Thus, a negative exponent tells us how many times to divide by ten. Dividing by ten, of course, can be done by simply moving the decimal point. Thus, 1.4×10^{-4} can be re-expressed as 0.00014. Notice that the decimal point is four places to the *left* of the 1. Here are some examples of numbers expressed as negative exponentials and their equivalents.

$$3567.9 \times 10^{-3} = 3.5679$$
$$0.01456 \times 10^{-2} = 0.0001456$$
$$45691 \times 10^{-3} = 45.691$$

To express a number smaller than 1 in scientific notation, we count the number of places the decimal has to be moved to put it to the right of the first nonzero digit. The number that we count equals the negative exponent. For example, you would have to move the decimal point five places to the right to put it to the right of the first nonzero digit in

$$0.\underbrace{00006}_{\text{5 places}}8901$$

This number can be re-expressed as 6.8901×10^{-5}.

Multiplying Numbers Written in Exponential and Scientific Notation

The real value of exponential forms of numbers comes in carrying out multiplications and divisions of large and small numbers. Suppose we want to multiply 1000 by 10000. Doing this by a long process fills the page with zeros (and some ones). But notice the following relationships.

Numbers	1000	×	10000		
	[10 × 10 × 10]	×	[10 × 10 × 10 × 10]	=	10,000,000
Exponential form	10^3	×	10^4	=	10^7
Exponents	3	+	4	=	7

If we *add* 3 and 4, the exponents of the exponential forms of 1000 and 10000, we get the exponent for the answer. Suppose we want to multiply 4160 by 20000. If we re-express each number in scientific notation we have

Multiply these parts.

$$(4.16 \times 10^3) \times (2.00 \times 10^4)$$

Multiply these parts.

This now simplifies to

$$(4.16 \times 2.00) \times [10^3 \times 10^4]$$

The answer can be easily worked without losing the location of the decimal point. The exponents are added to give the exponent on 10 in the answer, and the numbers 4.16 and 2.00 are multiplied. The product is 8.32×10^7. Thus there are two steps in multiplying numbers that are written in scientific notation.

1. Multiply the decimal parts of the numbers (the parts that precede the 10s).
2. Add the exponents of the 10s algebraically to obtain the exponent on the 10 in the answer.

Dividing Numbers Written in Exponential or Scientific Notation

Suppose we want to divide 10,000,000 by 1000. Doing this by long division would be primitive to say the least. It is much easier using exponential notation, where 10,000,000 = 10^7 and 1000 = 10^3. Notice the following relationships.

$$\frac{10{,}000{,}000}{1000} = 10{,}000 \qquad \frac{10^7}{10^3} = 10^4 = 10{,}000$$

The exponent in the result is (7 – 3). So, to divide numbers in exponential form, we subtract the exponent on 10 in the denominator from the exponent on 10 in the numerator.

To extend this operation one step, let's divide 0.00468 by 0.0000400. The answer can be obtained as follows, expressing the numbers in scientific notation.

$$\frac{4.68 \times 10^{-3}}{4.00 \times 10^{-5}} = \frac{4.68}{4.00} \times 10^{[(-3)-(-5)]}$$
$$= 1.17 \times 10^2$$

Notice that the division proceeds in two steps.

1. Carry out the division of the numbers standing before the 10s.
2. Algebraically subtract the exponent in the denominator from the exponent in the numerator.

Estimating Answers by Mental Arithmetic

Often, in working out chemistry problems, we find it necessary to perform a series of multiplications and divisions. These calculations are most easily handled using a calculator, but to check the answer quickly, we can do some simple mental arithmetic. For example, suppose that in solving a problem we performed the following arithmetic.

$$\frac{(1.908 \times 10^3) \times (4.56 \times 10^{-3}) \times (4.52 \times 10^7)}{(1.664 \times 10^{-1}) \times (2.34 \times 10^9) \times (3.02 \times 10^2)} = 3.34 \times 10^{-3} \text{ (rounded)}$$

To perform a check on the arithmetic to see whether the answer is "in the right ball park," we first separate the powers of ten from the other numbers. (You don't actually have to rewrite the problem setup; we're doing so here to make the procedure clearer.)

$$\frac{(1.908) \times (4.56) \times (4.52)}{(1.664) \times (2.34) \times (3.02)} \times \frac{(10^{3}) \times (10^{-3}) \times (10^{7})}{(10^{-1}) \times (10^{9}) \times (10^{2})}$$

Next, let's check the exponential part of the calculation by combining the powers of 10.

$$\begin{aligned} \text{exponential part} &= 10^{[(3-3+7)-(-1+9+2)]} \\ &= 10^{-3} \end{aligned}$$

This agrees with the results obtained with the calculator, so we know our answer is not unreasonable. If we want to check the rest of the math, we need to estimate the results of the arithmetic involving the pre-exponential parts of the numbers

$$\frac{(1.908) \times (4.56) \times (4.52)}{(1.664) \times (2.34) \times (3.02)}$$

We do this by rounding off the numbers so we can do the arithmetic in our heads. Let's round 1.908 to 2. The next two numbers are both close to 4.5, so we will round one of them down and the other up, hoping to cancel rounding errors: 4.56 becomes 4 and 4.52 becomes 5. Similar rounding applied to the numbers in the denominator gives us the following:

$$\frac{(1.908) \times (4.56) \times (4.52)}{(1.664) \times (2.34) \times (3.02)} \approx \frac{2 \times 4 \times 5}{2 \times 2 \times 3} = \frac{40}{12} = \frac{10}{3} \approx 3.3$$

So, our rough arithmetic gives us an answer of 3.3×10^{-3}, which is almost exactly the answer we obtained using the calculator.

Adding or Subtracting Numbers in Scientific Notation

The important thing to remember here is that to perform the arithmetic, both numbers must have the same power of 10. If they're not given that way, then you have to convert one to have the same exponent on 10 as the other. For example, suppose we had to add the two measured distances, 2.36×10^{5} cm and 5.08×10^{3} cm. We could change 5.08×10^{3} cm to have the exponential part equal 10^{5}, or we could change 2.36×10^{5} cm to have the exponential part equal 10^{3}.

$$\begin{array}{lcr} 2.36 \times 10^{5} & \qquad & 236 \times 10^{3} \\ \underline{0.0508 \times 10^{5}} & & \underline{5.08 \times 10^{3}} \\ 2.41 \times 10^{5} & & 241 \times 10^{3} \end{array}$$

Notice that in both cases, we have applied the rules for significant figures as they apply to addition and subtraction, given on page 44.

A.2 | Logarithms

A **logarithm** is simply an exponent. For example, if we have an expression

$$N = a^{b}$$

we see that to obtain N we must raise a to the b power. The exponent b is said to be the logarithm of N; it is the exponent to which we must raise a, which we call the *base*, to obtain the number N.

$$\log_a N = b$$

We can define a logarithm system for any base we want. For example, if we choose the base 2, then

$$\log_2 8 = 3$$

which means that to obtain the number 8, we must raise the base (2) to the third power.

$$8 = 2^3$$

The most frequently encountered logarithm systems in the sciences are *common logarithms* and *natural logarithms*, which are discussed separately below. However, for any system of logarithms there are some useful relationships that evolve from the behavior of exponents in arithmetic operations. We encounter these at various times throughout the sciences, so it is important that you are familiar with them.

For Multiplication:

$$\begin{aligned} &\text{If} && N = A \times B \\ &\text{then} && \log N = \log A + \log B \end{aligned}$$

For Division:

$$\begin{aligned} &\text{If} && N = \frac{A}{B} \\ &\text{then} && \log N = \log A - \log B \end{aligned}$$

For Exponentials:

$$\begin{aligned} &\text{If} && N = A^b \\ &\text{then} && \log N = b \log A \end{aligned}$$

Common Logarithms

The **common logarithm** or **log$_{10}$** of a number N is the exponent to which 10 must be raised to equal the number N. Thus, if

$$N = 10^x$$

then the common logarithm of N, or **log$_{10}$ N**, is simply x.

$$\log_{10} N = \log N = x$$

As mentioned earlier, there is another kind of logarithm called a **natural logarithm** that we'll take up later. However, when we use the terms "logarithm" or "log N" without specifying the base, we always mean common logarithms related to the base 10, as indicated above.

If N is just 10 raised to a power, finding the logarithm is simple. For example, suppose we want to find the logarithm of 10^{18}.

$$\log 10^{18} = ?$$

This expression is asking, "To what power do we raise 10 to obtain 10^{18}?" The answer, of course, is 18. (We have to raise 10 to the power 18 to obtain 10^{18}.)

$$\log 10^{18} = 18$$

Here are a few more examples.

$$\begin{aligned} N &= 10 = 10^1 & \log N &= 1 \\ &= 100 = 10^2 & &= 2 \\ &= 0.1 = 10^{-1} & &= -1 \\ &= 0.0001 = 10^{-4} & &= -4 \end{aligned}$$

The logarithms of these numbers were easy to figure out by just using the definition of logarithms, but usually it isn't this simple. For example, what is the value of x in the following equations?

$$4.23 = 10^x$$
$$\log 4.23 = x$$

In other words, to what power of x must we raise 10 to obtain 4.23? Obviously, the exponent is not a whole number. Therefore, to determine the value of x we use a scientific calculator. We will have more to say about this in Section A.5.

Natural Logarithms

In the sciences there are many phenomena in which observed quantities are related to each other logarithmically, which means that there is an exponential relationship between them. However, this exponential relationship does not involve 10 raised to a power. Instead it involves powers of a number symbolized by the letter e, which is said to be the base of the system of natural logarithms.

The quantity e is derived from calculus and is an irrational number, just like another quantity you are familiar with, π. This means that e is a nonrepeating decimal. To eight significant figures its value is

$$e = 2.7182818\ldots$$

To truly appreciate the significance of this number and the system of logarithms based on it, you must have a good foundation in calculus. A discussion of calculus is beyond the scope of this text, so we will not attempt to explain the origin of the value of e further. Nevertheless, we can still use the results and discuss the system of **natural logarithms** that has the number e as its base.

Natural logarithms use the symbol **ln** instead of log. Thus, if the number N equals e^x,

$$N = e^x$$

then

$$\log_e N = \ln N = x$$

Scientific calculators have the ability to calculate natural logarithms and their corresponding *antilogarithms*. This is discussed in Section A.5 of this appendix. There is a simple relationship between common and natural logarithms. To four significant figures,

$$\ln N = 2.303 \log N$$

In other words, to find $\ln N$, simply find the common log of N and multiply it by 2.303.

A.3 | Graphing

One of the most useful ways of describing the relationship between two quantities is by means of a graph. It allows us to obtain an overall view of how one quantity changes when the other changes. Constructing graphs from experimental data, or from data calculated from an equation, is therefore a common operation in the sciences, so it is important that you understand how to present data graphically. Let's look at an example.

Suppose that we wanted to know how the volume of a given amount of gas varies as we change its pressure. In Chapter 11 we find an equation that gives the pressure–volume relationship for a fixed amount of gas at a constant temperature,

$$PV = \text{constant} \qquad \textbf{(A.1)}$$

where $P =$ pressure and $V =$ volume. For calculations, this equation can be used in two ways. If we solve for the volume, we get

$$V = \frac{\text{constant}}{P} \tag{A.2}$$

Knowing the value of the constant for a given gas sample at a given temperature allows us to calculate the volume that the gas occupies at any particular pressure. Simply substitute in the values for the constant and the pressure and compute the volume.

Equation A.1 can also be solved for the pressure.

$$P = \frac{\text{constant}}{V} \tag{A.3}$$

From this equation the pressure corresponding to any particular volume can be calculated.

Now, suppose, that we want to see graphically how the pressure and volume of a gas are related as the pressure is raised from 1.0 to 10.0 atm in steps of 1.0 atm. Let's also suppose that for this sample of gas the value of the constant in our equation is 0.25 L atm. To construct the graph we first must decide how to label and number the axes.

Usually, the horizontal axis, called the **abscissa**, is chosen to correspond to the **independent variable**—the variable whose values are chosen first and from which the values of the **dependent variable** are determined. In our example, we are choosing values of pressure (1.0 atm, 2.0 atm, etc.), so we will label the abscissa "pressure." We will also mark off the axis evenly from 1.0 to 10.0 atm, as shown in Figure A.1. Next we put the label "volume" on the vertical axis (the ordinate). Before we can number this axis, however, we need to know over what range the volume will vary. Using Equation A.2 we can calculate the data in Table A.2, and we see that the volume ranges from a low of 0.025 L to a high of 0.25 L. We can therefore mark off the ordinate evenly in increments of 0.025 L, starting at the bottom with 0.025 L. Notice that in labeling the axes we have indicated the units of P and V in parentheses.

Next we plot the data as shown in Figure A.2. To clearly show each plotted point, we use a small circle that has its center located at the coordinates of the point. Then we draw a *smooth* curve through the points.

Sometimes, when plotting experimentally measured data, the points do not fall exactly on a smooth line (Figure A.3). However, nature generally is not irregular even though that's what the data appear to suggest. The fluctuations are usually due to experimental error of some sort. Therefore, rather that draw an irregular line connecting all the data points (the dashed line), we draw a smooth curve that passes as close as possible to all of the points, even though it may not actually pass through any of them.

Table A.2

Pressure (atm)	Volume (L)
1.0	0.25
2.0	0.125
3.0	0.083
4.0	0.062
5.0	0.050
6.0	0.042
7.0	0.036
8.0	0.031
9.0	0.028
10.0	0.025

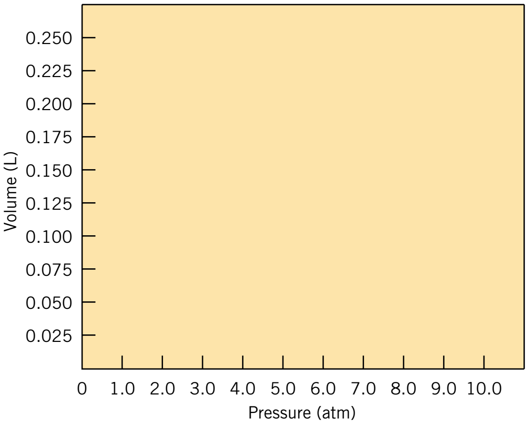


Figure A.1 | Choosing and labeling the axes of a graph.

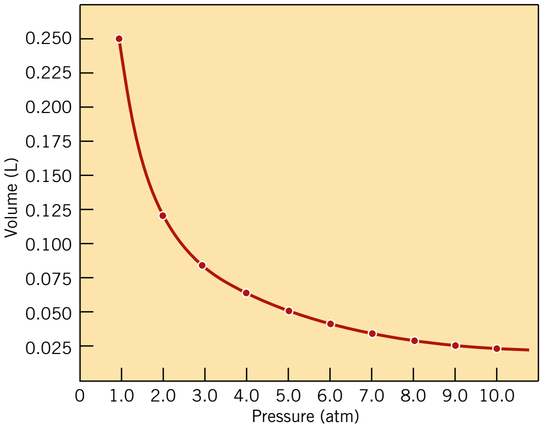


Figure A.2 | Plotting points and drawing the curve.

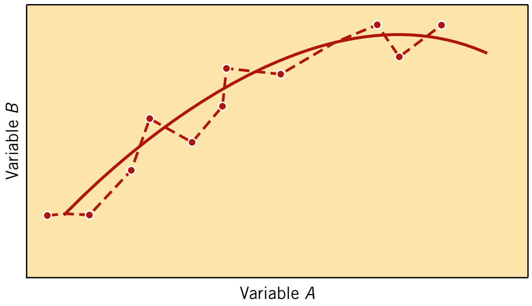


Figure A.3 | Experimental data do not all fall on a smooth curve when they are plotted because they contain experimental error. A smooth curve is drawn as close to all of the data points as possible, rather than the jerky dashed line.

Slope

One of the properties of curves and lines on a graph is their *slope* or steepness. Consider Figure A.4, which is a straight line drawn on a set of xy coordinate axes. The slope of the line is defined as the change in y, Δy, divided by the change in x, Δx.

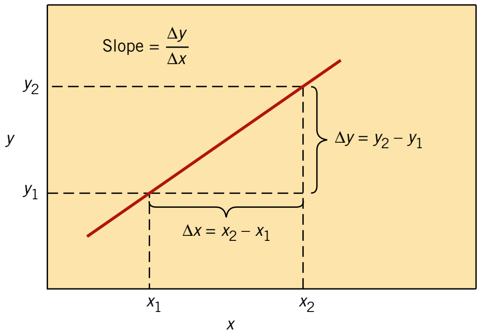


Figure A.4 | Determining the slope of a straight line. Two points are chosen on the line and Δx and Δy are determined. The ratio $\Delta x/\Delta y$ is the slope of the line.

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

Curved lines have slopes too, but the slope changes from point to point on the curve. To obtain the slope graphically, we can draw a line that is tangent to the curve at the point where we want to know the slope. The slope of this tangent is the same as the slope of the curve at this point. In Figure A.5 we see a curve for which the slope is determined at two different points. At point M the curve is rising steeply and $\Delta y/\Delta x$ for the tangent is large. At point N the curve is rising less steeply, and $\Delta y/\Delta x$ for the tangent at N is small. Therefore, the slope at M is larger than the slope at N.

Straight Line Graphs

A type of graph that scientists find especially useful is a straight line graph—one similar to Figure A.4. A straight line is obtained when we plot an equation with the general form

$$y = mx + b$$

where m is the slope of the line and b is the intercept of the line with the y axis (where $x = 0$). Usually, the experimental data correspond to the x and y values. When the data are plotted, the slope and intercept can be obtained from the graph. Let's look at an example.

In Figure A.2 we plotted the P-V data in Table A.2. Pressure and volume for a gas are related by the following equation, obtained by solving Equation A.1 for P.

$$P = \frac{\text{constant}}{V} \tag{A.4}$$

Let's rewrite this equation as follows, noting it's similarity of the equation for a straight line.

$$\begin{array}{cccccc} P = & (\text{constant}) & \dfrac{1}{V} & + & 0 \\ \downarrow & \downarrow & \downarrow & & \downarrow \\ y = & m & x & + & b \end{array}$$

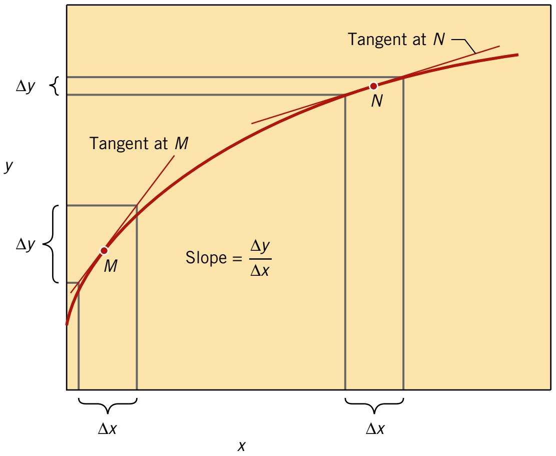


Figure A.5 | For a given Δx, Δy is much larger at M than it is at N. Therefore, the slope at M is larger than at N.

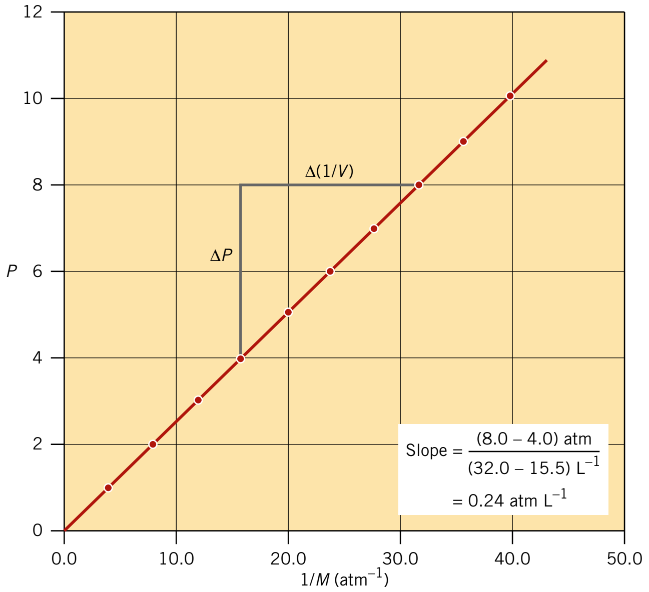


Figure A.6 | A graph of P versus $1/V$.

Table A.3 **Data for a graph of P versus 1/V using values from Table A.2**

P (atm)	$1/V$ (L^{-1})
1	4.0
2	8.0
3	12.0
4	16.1
5	20.0
6	23.8
7	27.8
8	32.3
9	35.7
10	40.0

This tells us that if we plot P versus $1/V$, we should obtain a straight line with a slope that's equal to the constant in Equation A.4, and with an intercept of zero (i.e., the line should pass through zero). Table A.3 contains P and $1/V$ data obtained from the data in Table A.2. These data are plotted in Figure A.6. The slope of the line is obtained as described in Figure A.4 by choosing two points on the graph, estimating x and y values, and calculating the slope. The results are also shown in Figure A.6.

Sometimes the relationship between x and y is as follows,

$$y = A\,e^{Bx}$$

where e is the base of the natural logarithm system. In such situations, we take the natural logarithm of both sides of the equation,

$$\ln y = \ln A + B\,x$$

which we can rearrange as

$$\begin{array}{cccccc} \ln y & = & B & x & + & \ln A \\ \downarrow & & \downarrow & \downarrow & & \downarrow \\ y & = & m & x & + & b \end{array}$$

Notice how we have once again obtained an equation that follows the form of a straight line, so by plotting $\ln y$ versus x, we should obtain a straight line with a slope equal to B and an intercept of $\ln A$.

A.4 | Method of Successive Approximations

This section of the appendix applies primarily to problems associated with Chapters 15 and 17 where we discuss problems involved with chemical equilibria.

In nearly all of the examples described in Chapter 17, simplifications in the algebra are possible because K_a or K_b are very small and the concentration of the solute is relatively large. However, there are instances when the simplifications are not justified and other methods are needed to solve the algebra. For example, suppose that in working a problem dealing with a weak acid equilibrium we reach the point where we have to solve the following equation for *x*.

$$\frac{x^2}{(0.010 - x)} = 1.4 \times 10^{-3} \tag{A.5}$$

For this problem, the usual simplifications do not work, so we are not justified in assuming that $(0.010 - x) \approx 0.010$. As a result, we have to deal with solving a quadratic equation. There are two ways to go about it. In one approach, we solve for *x* using the quadratic formula, as described on page 725. For Equation A.5, applying the quadratic formula yields $x = 3.1 \times 10^{-3}$.

The second approach is to apply a procedure called the *method of successive approximations.* This method is not only much faster than using the quadratic formula, particularly with a scientific calculator, but it is also just as accurate. The procedure is outlined in Figure A.7, which you should follow as we apply the method to solving Equation A.5 for *x*.

Step 1 We apply the simplifying approximation to Equation A.5, even though we know it is not really applicable. Doing this, we obtain the following:

$$\frac{x^2}{(0.010 - x)} \approx \frac{x^2}{0.010} = 1.4 \times 10^{-3}$$

for which we obtain the solution $x = 3.7 \times 10^{-3}$. We call this quantity, $x = 3.7 \times 10^{-2}$, our *first approximation.*

Step 2 We substitute $x = 3.7 \times 10^{-3}$ (our first approximation) into the term in the denominator, $(0.100 - x)$, and then recompute *x*. This gives us

$$\frac{x^2}{(0.010 - 0.0037)} = 1.4 \times 10^{-3}$$

or

$$x^2 = (0.006) \times 1.4 \times 10^{-3}$$

Taking only the positive root,

$$x = 2.9 \times 10^{-3} \ (\textit{second approximation})$$

We call $x = 2.9 \times 10^{-3}$ our *second approximation.*

Step 3 We compare the second approximation to the first and we see they are not the same, so we repeat Step 2.

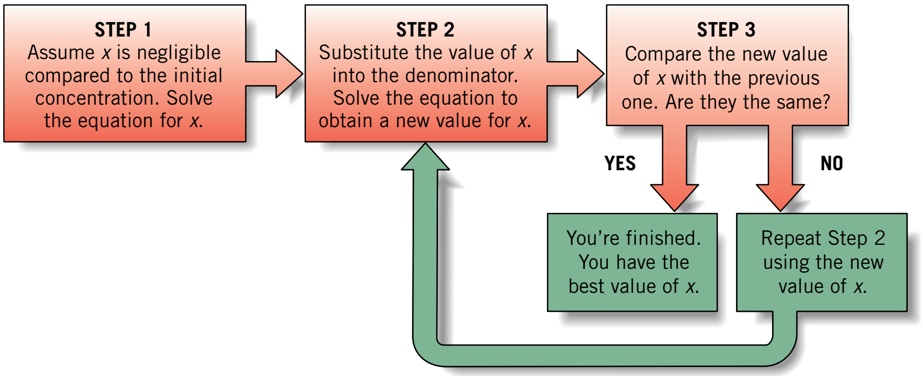

STEP 1
Assume x is negligible compared to the initial concentration. Solve the equation for x.
STEP 2
Substitute the value of x into the denominator. Solve the equation to obtain a new value for x.
STEP 3
Compare the new value of x with the previous one. Are they the same?
YES
NO
You're finished. You have the best value of x.
Repeat Step 2 using the new value of x.

Figure A.7 | Steps in the method of successive approximations.

Step 2 again We substitute $x = 2.9 \times 10^{-3}$ (our second approximation) into the term in the denominator, $(0.100 - x)$, and then recompute x. This gives us a *third approximation*,

$$\begin{aligned} \frac{x^2}{(0.010 - 0.0029)} &= 1.4 \times 10^{-3} \\ x^2 &= (0.007) \times 1.4 \times 10^{-3} \\ x &= 3.1 \times 10^{-3} \quad (\textit{third approximation}) \end{aligned}$$

Step 3 again The third approximation is not the same as the second approximation, so we repeat Step 2 again.

Step 2 again We substitute $x = 3.1 \times 10^{-3}$ (our third approximation) into the term in the denominator, $(0.100 - x)$, and then recompute x. This gives us

$$\begin{aligned} \frac{x^2}{(0.010 - 0.0031)} &= 1.4 \times 10^{-3} \\ x^2 &= (0.007) \times 1.4 \times 10^{-3} \\ x &= 3.1 \times 10^{-3} \quad (\textit{fourth approximation}) \end{aligned}$$

Step 3 again When we compare the third and fourth approximations, we see that they are identical, so we are finished. The method of successive approximations tells us that $x = 3.1 \times 10^{-3}$.

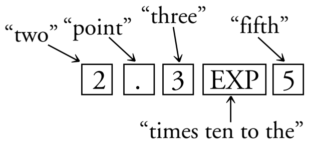
First, you might notice that the answer obtained by the method of successive approximations is identical to that obtained using the quadratic formula (which also gave $x = 3.1 \times 10^{-3}$). Also notice that the second pass through Step 2 gave a smaller correction than the first. Each succeeding approximation differs from the preceding one by a smaller and smaller amount. We stop the calculation when the difference between two approximations is insignificant. Try this approach by working Problem 17.131 on page 827.

A.5 | Tips on Using Scientific Calculators

Scientific Calculators and Scientific Notation

Scientific calculators give you the ability to easily perform arithmetic of all kinds, and they are especially useful when you have to deal with large or small numbers expressed as exponentials. As you would expect, addition, subtraction, multiplication, and division are performed with the keys $\boxed{+}$, $\boxed{-}$, $\boxed{\times}$, and $\boxed{\div}$, respectively.[1] However, students often have difficulty in properly entering numbers in scientific notation, so let's take a detailed look at this.

To deal with numbers in scientific notation, such as 2.3×10^5 or 6.7×10^{-12}, calculators have a special key often labeled EXP or EE. If we read the number 2.3×10^5 as "two point three times ten to the fifth," the EXP (or EE) key should be read as ". . . times ten to the . . ." Thus the sequence of keys that enter the number 2.3×10^5 is



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[1] You're probably familiar with the old adage: "When all else fails, read the instructions!" We strongly encourage you to read the *Instruction Manual* that came with your calculator.

Try this on your own calculator and check to be sure that the number is correctly displayed after you've entered it.[2] If not, check the instruction booklet that came with the calculator or ask your instructor for help.

When entering a number such as 6.7×10^{-12}, be sure to press the "change sign" or "+/−" key after pressing the EXP key. Calculators will not give the correct entry if the "minus" key is pressed instead of the "+/−" key. For example, clear the display and then try the following sequence of keystrokes on your calculator.

$$\boxed{6}\ \boxed{.}\ \boxed{7}\ \boxed{\text{EXP}}\ \boxed{+/-}\ \boxed{1}\ \boxed{2}$$

If you wish to multiply these two numbers together, enter the first one, press the $\boxed{\times}$ key, then enter the second number, and finally press the $\boxed{=}$ key. The answer displayed on the calculator should be 1.541×10^{-6}.

$$(2.3 \times 10^{5}) \times (6.7 \times 10^{-12}) = 1.541 \times 10^{-6}$$

Chain Calculations

It is not uncommon to have to calculate the value of a fraction in which there is a string of numbers that must be multiplied together in the numerator and another string of numbers to be multiplied together in the denominator. For example,

$$\frac{5.0 \times 7.3 \times 8.5}{6.2 \times 2.5 \times 3.9}$$

Many students will compute the value of the numerator and write down the answer, then compute the value of the denominator and write it down, and finally divide the value of the numerator by the value of the denominator (whew!). Although this gives the correct answer, there is a simpler way to do the arithmetic that doesn't require writing down any intermediate values. The procedure is as follows:

1. Enter the first value from the numerator (5.0).
2. Any of the other values from the numerator are entered by *multiplication* and any of the values from the denominator are entered by *division*.

The following is one sequence that gives the answer.

$$5.0 \times 7.3 \times 8.5 \div 6.2 \div 2.5 \div 3.9 = 5.13234\ldots$$

Notice that each value from the denominator is entered by division. It also doesn't matter in what sequence the numbers are entered. The following gives the same answer.

$$5.0 \div 6.2 \times 7.3 \div 2.5 \div 3.9 \times 8.5 = 5.13234\ldots$$

Logarithms and Antilogarithms

Your scientific calculator works with both common logarithms and natural logarithms. To find the common log of a number, enter the number in the calculator and press the $\boxed{\text{log}}$ or $\boxed{\text{LOG}}$ button. Try this for the following and check your results. (The values here are rounded so they have the same number of digits after the decimal point as there are significant figures in the number. This is the rule for significant figures in logarithms as described below):

$$\log 12.35 = 1.0917 \text{ (rounded)}$$

$$\log (3.70 \times 10^{-4}) = -3.432 \text{ (rounded)}$$

---

[2] Sometimes students make the mistake of trying to enter a number such as 2.3×10^{5} as follows: $\boxed{2}\ \boxed{.}\ \boxed{3}\ \boxed{\times}\ \boxed{1}\ \boxed{0}\ \boxed{\text{EXP}}\ \boxed{5}$. What this series of operations accomplishes is to multiply 2.3 by 10, giving 23, and then entering the exponential notation 10^{5}.

$$\boxed{2}\ \boxed{.}\ \boxed{3}\ \boxed{\times}\ \boxed{1}\ \boxed{0}\ \boxed{\text{EXP}}\ \boxed{5} = 23 \times 10^{5}$$

This is certainly not what was intended. If you are doing arithmetic and your answers are off by powers of 10, check to be sure you're entering the numbers correctly into the calculator.

Obtaining the antilogarithm is equally easy. For the first number above, 12.35 is the antilog of 1.0917, which means that

$$12.35 = 10^{1.0917}$$

Some calculators have a key labeled $\boxed{10^x}$; others use a combination of an inverse function key, usually labeled $\boxed{\text{INV}}$, and the key used to obtain the logarithm. Thus, entering the value 1.0917 and pressing either $\boxed{10^x}$ or the sequence $\boxed{\text{INV}}$ $\boxed{\text{log}}$ yields the value 12.35. Try it.

To obtain natural logarithms of a number we use key labeled either $\boxed{\ln x}$ or $\boxed{\text{LN}}$ or sometimes $\boxed{\ln}$. Thus the natural logarithm of 12.35 is obtained by entering the number and pressing the $\boxed{\ln x}$ key. Try it.

$$\ln 12.35 = 2.5137 \text{ (rounded)}$$

The value 12.35 is the antinatural logarithm (antiln) of 2.5137, which means

$$12.35 = e^{2.5137}$$

Therefore, to obtain the antilogarithm of 2.5137, we enter the number into the calculator and press either the key labeled $\boxed{e^x}$ or the sequence $\boxed{\text{INV}}$ $\boxed{\ln x}$. Try it.

$$\text{antiln } 2.5137 = 12.35$$

Significant Figures and Logarithms

The logarithm of a number is composed of two parts. There is a part that comes before the decimal point (which is called the *characteristic*) and a part that comes after the decimal point (which is called the *mantissa*). Let's look at an example, for the moment keeping all the digits shown on the calculator.

$$\log(4.23 \times 10^5) = \overset{\text{characteristic}}{5}.\underbrace{626340367}_{\text{mantissa}}$$

The characteristic comes from the exponent on the 10 ($\log 10^5 = 5$) and is an exact number, so it need not be considered for the purposes of significant figures. The mantissa, on the other hand, is the logarithm of the number that precedes the power of ten [$\log(4.23) = 0.626340367$]. The 4.23 has three significant figures, so the mantissa should also have three significant figures. Therefore, rounded correctly,

$$\log(4.23 \times 10^5) = 5.626 \text{ (rounded)}$$

This leads to the rule that *when we take the logarithm of a quantity, the number of decimal places shown in the logarithm should equal the number of significant figures in the quantity*. Here is another example.

$$\begin{aligned} \log(5.246 \times 10^{-7}) &= -6.280171714 \\ &= -6.2802 \text{ (rounded correctly)} \end{aligned}$$

The quantity 5.246×10^{-7} has four significant figures, so we round off the logarithm to the fourth decimal place.

When taking an antilogarithm, the same relationship applies. If we take the antilog of 6.557, the answer will have three significant figures because the logarithm has three digits after the decimal.

$$\text{antilog}(6.557) = 3.61 \times 10^6 \text{ (rounded correctly)}$$

The same rules for significant figures apply for both common and natural logarithms.

Powers and Roots

Squares and square roots are handled easily with keys labeled $\boxed{x^2}$ and $\boxed{\sqrt{x}}$. For higher powers and higher roots (e.g., cube roots or fourth roots) we use the key that on most scientific calculators is labeled $\boxed{x^y}$. To use this function, we must enter two values—the number and its exponent. For example, to raise the number 2.6 to the 5th power,

$$(2.6)^5$$

we enter the number 2.6, press the $\boxed{x^y}$ key enter the value of the exponent (5), and then press either the "equals" key or the next function key desired if we are performing a chain calculation. Thus, the sequence

$$\boxed{2}\ \boxed{.}\ \boxed{6}\ \boxed{x^y}\ \boxed{5}\ \boxed{=}$$

produces the result 118.81376 on the display of the calculator. Therefore,

$$(2.6)^5 = 118.81376$$

To take a root, the procedure is quite similar, because we make use of the relationship

$$\sqrt[n]{(\text{number}} = (\text{number})^{1/n}$$

Thus, the cube root of a number such as 56.4 is obtained as

$$\sqrt[3]{56.4} = (56.4)^{1/3} = (56.4)^{0.333333\ldots}$$

In other words, we raise 56.4 to the one-third power, for which the decimal equivalent is 0.3333333 … (with as many threes as will fit on the display). Let's try it. Clear the display and enter the number 56.4. Next, press the $\boxed{x^y}$ key. Then enter 0.33333 with as many threes after the decimal point as you can. Finally, press the "equals" key. The answer should be 3.834949 …. If we had wanted to take the 5th root of 56.4, we would raise the number to the 1/5 power, or 0.20. Try it. You should get 2.24004 … as the answer.

Some calculators have a key labeled $\boxed{x^{1/y}}$, which makes taking a root even easier. Thus, to take the 5th root of 56.4, we would enter the number 56.4, then press the $\boxed{x^{1/y}}$ key, and then press 5. Once again, the answer displayed should be 2.24004.

Appendix B

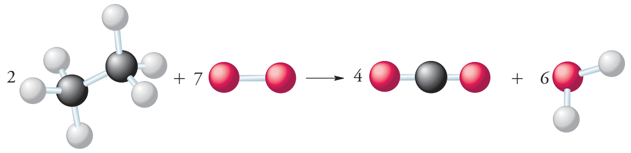
Answers to Practice Exercises and Selected Review Problems

Chapter 1

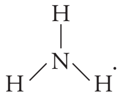
Practice Exercises

1.1 **(a)** 1 S, 6 F **(b)** 4 C, 12 H, 2 N **(c)** 3 Ca, 2 P, 8 O **(d)** 1 Co, 2 N, 12 O, 12 H. **1.2** **(a)** 2 N nitrogen, 4 H hydrogen, 3 O oxygen. **(b)** 1 Fe iron, 1 N nitrogen, 4 H hydrogen, 2 S sulfur, 8 O oxygen. **(c)** 1 Mo molybdenum, 2 N nitrogen, 11 O oxygen, 10 H hydrogen. **(d)** 6 C carbon, 4 H hydrogen, 1 Cl chlorine, 1 N nitrogen, 2 O oxygen. **1.3** C_2H_7N, CH_3NHCH_3. **1.4** Reactants: 4 N, 12 H, and 6 O; Products: 4 N, 12 H, and 6 O. **1.5** Reactants: 6 N, 42 H, 2 P, 20 O, 3 Ba, 12 C; Products: 3 Ba, 2 P, 20 O, 6 N, 42 H, 12 C; Reaction is balanced.

1.6



Review Problems

1.30 1 Cr, 6 C, 9 H, 6 O. **1.32** $MgSO_4$. **1.34** CH_3COOH or $C_2H_4O_2$. **1.36** NH_3. **1.38** **(b)**  $\mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H}$. **1.40** **(a)** 2 K potassium, 2 C carbon, 4 O oxygen. **(b)** 2 H hydrogen, 1 S sulfur, 3 O oxygen. **(c)** 12 C carbon, 26 H hydrogen. **(d)** 4 H hydrogen, 2 C carbon, 2 O oxygen. **(e)** 9 H hydrogen, 2 N nitrogen, 1 P phosphorus, 4 O oxygen. **1.42** **(a)** 1 Ni nickel, 2 Cl chlorine, 8 O oxygen. **(b)** 1 C carbon, 1 O oxygen, 2 Cl chlorine **(c)** 2 K potassium, 2 Cr chromium, 7 O oxygen. **(d)** 2 C carbon, 4 H hydrogen, 2 O oxygen. **(e)** 2 N nitrogen, 9 H hydrogen, 1 P phosphorus, 4 O oxygen. **1.44** **(a)** 6 N, 3 O **(b)** 8 C, 24 H, 4 S **(c)** 2 Cu, 2 S, 18 O, 20 H **1.46** $C_2H_6O_2$, C_3H_6O These two compounds illustrate that different masses of carbon combine with the same mass of hydrogen and those masses are in small, whole-number ratios. It is also true for the ratio of oxygen to a fixed mass of hydrogen.
1.48 **(a)** 6. **(b)** 3 **(c)** 27 **(d)** 2
1.50 $2S(CH_3)_2$, 9 O_2, 2 SO_2, 4 CO_2, 6 H_2O
$2S(CH_3)_2(g) + 9\,O_2(g) \longrightarrow 2\,SO_2(g) + 4\,CO_2(g) + 6\,H_2O(l)$.
1.52 Reaction is not balanced as written, $2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$.

Chapter 2

Practice Exercises

2.1 meters^3 or m^3. **2.2** $\mathrm{kg}\frac{m}{s^2}$ or kg m s^{-2}. **2.3** 187 °C. **2.4** 10 °C, 293 K. **2.5** **(a)** 42.0 g, **(b)** 0.857 g/mL, **(c)** 149 cm. **2.6** **(a)** 30.0 mL, **(b)** 54.155 g, **(c)** 11.3 g, **(d)** 3.62 ft, **(e)** 0.48 m^2. **2.7** 11.5 m^2. **2.8** **(a)** 108 in., **(b)** 1.25×10^5 cm, **(c)** 0.0107 ft, **(d)** 8.59 km L^{-1}. **2.9** $d = 16.5$ g cm^{-3}. The object is not composed of pure gold. **2.10** 647 lb. **2.11** 0.899 g/cm^3. **2.12** 0.0639 cm^3

Review Problems

2.26 **(a)** 0.01 m, **(b)** 1000 m, **(c)** 10^{12} pm, **(d)** 0.1 m, **(e)** 0.001 kg, **(f)** 0.01 g **2.28** **(a)** 135 °F, **(b)** 61 °F, **(c)** –3.61 °C, **(d)** 9.4 °C, **(e)** 335 K, **(f)** 242 K. **2.30** 39.7 °C This dog has a fever; the temperature is out of normal canine range. **2.32** Range in Celsius: 1.0×10^7 °C to 2.5×10^7 °C, Range in Fahrenheit: 1.8×10^7 °F to 4.5×10^7 °F. **2.34** −269 °C **2.36** **(a)** 4 significant figures, **(b)** 5 significant figures, **(c)** 4 significant figures, **(d)** 2 significant figures **(e)** 4 significant figures, **(f)** 2 significant figures
2.38 **(a)** 0.72 m^2, **(b)** 84.24 kg, **(c)** 4.19 g/cm^3, **(d)** 19.42 g/mL, **(e)** 858.0 cm^2 **2.40** **(a)** 11.5 km/h, **(b)** 8.2×10^6 μg/L, **(c)** 7.53×10^{-5} kg, **(d)** 0.1375 L, **(e)** 25 mL, **(f)** 3.42×10^{-20} dm
2.42 **(a)** 91 cm, **(b)** 2.3 kg, **(c)** 2800 mL, **(d)** 200 mL, **(e)** 88 km.hr, **(f)** 80.4 km **2.44** **(a)** 7,800 cm^2, **(b)** 577 km^2 **(c)** 6.54×10^6 cm^3
2.46 4,000 pistachios (don’t try this at home). **2.48** 90 m/s.
2.50 1520 mi/hr **2.52** 5.1×10^{13} mi **2.54** 11,034 m
2.56 0.798 g/mL **2.58** 31.6 mL **2.60** 276 g **2.62** 11 g/cm^3
2.64 Density = 0.591 lb/gal; 0.0709 g/mL,; specific gravity = 0.0708

Chapter 3

Practice Exercises

3.1 $^{240}_{94}$Pu, 94 electrons **3.2** 17 protons, 17 electrons, and 18 neutrons. **3.3** We can discard the 17 since the 17 tells the number of protons, which is information that the symbol “Cl” also provides. In addition, the number of protons equals the number of electrons in a neutral atom, so the symbol “Cl” also indicates the number of electrons. The 35 is necessary to state which isotope of chlorine is in question and therefore the number of neutrons in the atom.
3.4 26.9814 u **3.5** 5.2955 times as heavy as carbon **3.6** 10.8 u
3.7 20.2 u **3.8** **(a)** 26 protons, 26 electrons **(b)** 26 protons, 23 electrons **(c)** 7 protons, 10 electrons **(d)** 7 protons, 7 electrons
3.9 **(a)** 8 protons, 8 electrons **(b)** 8 protons, 10 electrons **(c)** 13 protons, 10 electrons **(d)** 13 protons, 13 electrons
3.10 **(a)** NaF **(b)** Na_2O **(c)** MgF_2 **(d)** Al_4C_3 **3.11** **(a)** Ca_3N_2 **(b)** $AlBr_3$ **(c)** K_2S **(d)** CsCl **3.12** **(a)** $CrCl_3$ and $CrCl_2$, Cr_2O_3 and CrO **(b)** CuCl, $CuCl_2$, Cu_2O and CuO **3.13** **(a)** Au_2S and Au_2S_3, Au_3N and AuN **(b)** TiS and TiS_2, Ti_3N_2 and Ti_3N_4 **3.14** **(a)** $KC_2H_3O_2$ **(b)** $Sr(NO_3)_2$ **(c)** $Fe(C_2H_3O_2)_3$ **3.15** **(a)** Na_2CO_3 **(b)** $(NH_4)_2SO_4$
3.16 **(a)** K_2S **(b)** $BaBr_2$ **(c)** NaCN **(d)** $Al(OH)_3$ **(e)** Ca_3P_2
3.17 **(a)** aluminum chloride **(b)** barium hydroxide **(c)** sodium bromide **(d)** calcium fluoride **(e)** potassium phosphide **3.18** lithium sulfide, magnesium phosphide, nickel(II) chloride, titanium(II) chloride, iron(III) oxide **3.19** **(a)** Al_2S_3 **(b)** SrF_2 **(c)** TiO_2 **(d)** CoO **(e)** Au_2O_3 **3.20** **(a)** lithium carbonate **(b)** potassium permanganate **(c)** iron(III) hydroxide **3.21** **(a)** $KClO_3$ **(b)** NaOCl

(c) $Ni_3(PO_4)_2$ **3.22** C_8H_{18}, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, **3.23** $C_{10}H_{22}$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$. **3.24** **(a)** Propanol: C_3H_8O, $CH_3CH_2CH_2OH$ **(b)** Butanol: $C_4H_{10}O$, $CH_3CH_2CH_2CH_2OH$ **3.25** **(a)** Phosphorus trichloride **(b)** sulfur dioxide **(c)** dichlorine heptoxide **(d)** hydrogen sulfide **3.26** **(a)** $AsCl_5$ **(b)** SCl_6 **(c)** S_2Cl_2 **(d)** H_2Te **3.27** Diodine pentoxide **3.28** Chromium(III) acetate **3.29** Potassium perchlorate

Review Problems

3.69 1.008 u **3.71** The element is Al **3.73** The ratio would not change. **3.75** 63.55 u **3.77** **(a)** 88 protons, 88 electrons, 138 neutrons **(b)** 82 protons, 82 electrons, 124 neutrons **(c)** 6 protons, 6 electrons, 8 neutrons **(d)** 11 protons, 11 electrons, 12 neutrons **3.79** 53 protons, 53 electrons, 78 neutrons **3.81** **(a)** K^+ **(b)**Br^- **(c)** Mg^{2+} **(d)** S^{2-} **(e)** Al^{3+} **3.83** **(a)** NaBr **(b)** KI **(c)** BaO **(d)** $MgBr_2$ **(e)** BaF_2 **3.85** **(a)** KNO_3 **(b)** $Ca(C_2H_3O_2)_2$ **(c)** NH_4Cl **(d)** $Fe_2(CO_3)_3$ **(e)** $Mg_3(PO_4)_2$ **3.87** **(a)** PbO and PbO_2 **(b)** SnO and SnO_2 **(c)** MnO and Mn_2O_3 **(d)** FeO and Fe_2O_3 **(e)** Cu_2O and CuO **3.89** **(a)** calcium sulfide **(b)** aluminum bromide **(c)** sodium phosphide **(d)** barium arsenide **(e)** rubidium sulfide **3.91** **(a)** silicon dioxide **(b)** xenon tetrafluoride **(c)** tetraphosphorus decoxide **(d)** dichlorine heptoxide **3.93** **(a)** Iron(II) sulfide **(b)** copper(II) oxide **(c)** tin(IV) oxide **(d)** cobalt(II) chloride hexahydrate **3.95** **(a)** sodium nitrite **(b)** potassium permanganate **(c)** magnesium sulfate heptahydrate **(d)** potassium thiocyanate **3.97** **(a)** ionic, chromium(II) chloride **(b)** molecular, disulfur dichloride **(c)** ionic, ammonium acetate **(d)** molecular, sulfur trioxide **(e)** ionic, potassium iodate **(f)** molecular, tetraphosphorus hexoxide **(g)** ionic, calcium sulfite **(h)** ionic, silver cyanide **(i)** ionic, zinc(II) bromide **(j)** molecular, hydrogen selenide **3.99** **(a)** Na_2HPO_4 **(b)** Li_2Se **(c)** $Cr(C_2H_3O_2)_3$ **(d)** S_2F_{10} **(e)** $Ni(CN)_2$ **(f)** Fe_2O_3 **(g)** SbF_5 **3.101** **(a)** $(NH_4)_2S$ **(b)** $Cr_2(SO_4)_3 \cdot 6H_2O$ **(c)** SiF_4 **(d)** MoS_2 **(e)** $SnCl_4$ **(f)** H_2Se **(g)** P_4S_7 **3.103** Diselenium hexasulfide and diselenium tetrasulfide

| Chapter 4

Practice Exercise

4.1 0.129 mol Al **4.2** $\pm 1.15 \times 10^{-5}$ mol K_2SO_4 **4.3** 0.00238 g **4.4** 3.5×10^{18} molecules of sucrose **4.5** 0.0516 mol Al^{3+} **4.6** 3.44 mol N atoms **4.7** 59.6 g Fe **4.8** 10.5 g Fe **4.9** 18.0 g Ti **4.10** % H = 13.04%, % C = 52.17; It is likely that the compound contains another element since the percentages do not add up to 100%. **4.11** % N = 36.84, % O = 63.16; Since these two values constitute 100%, there are no other elements present.

4.12 % N = 30.45, % O = 69.55

4.13 N_2O: % N = 63.65, % O = 36.34
NO: % N = 46.68, % O = 53.32
NO_2: % N = 30.45, % O = 69.55
N_2O_3: % N = 36.86, % O = 63.14
N_2O_4: % N = 30.45, % O = 69.55
N_2O_5: % N = 25.94, % O = 74.06

The compound N_2O_3 corresponds to the data in Practice Exercise 4.11. **4.14** NO **4.15** SO_2 **4.16** Al_2O_3 **4.17** N_2O_5 **4.18** Na_2SO_4 **4.19** C_9H_8O **4.20** CS_2 **4.21** CH_2O **4.22** $C_2H_4Cl_2$ and $C_6H_6Cl_6$ **4.23** N_2H_4

4.24 $3CaCl_2(aq) + 2K_3PO_4(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6KCl(aq)$

4.25 $2Ca(NO_3)_2(aq) + 2\ (NH_4)_3PO_4(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6NH_4NO_3(aq)$

4.26 3.38 mol O_2 **4.27** 0.183 mol H_2SO_4 **4.28** 78.5 g Al_2O_3 **4.29** 1.18×10^2 g CO_2 **4.30** 55.0 g CO_2, 34 g HCl remaining **4.31** 30.01 g NO **4.32** 36.78 g $HOOCC_6H_4O_2C_2H_3$, 83.5% **4.33** 30.9 g $HC_2H_3O_2$, 86.1% **4.34** The two-step process is the preferred process.

Review Problems

4.27 1:2, 1 mol N to 2 mol O **4.29** 2.59×10^{-3} mole Ta

4.31 **(a)** 6 atom C:11 atom H **(b)** 12 mole C:11 mole O
(c) 2 atom H:1 atom O **(d)** 2 mole H:1 mole O

4.33 1.05 mol Bi **4.35** 4.32 mol Cr

4.37 **(a)** $\left(\dfrac{2 \text{ mol Al}}{3 \text{ mol S}}\right)$ or $\left(\dfrac{3 \text{ mol S}}{2 \text{ mol Al}}\right)$

(b) $\left(\dfrac{3 \text{ mol S}}{1 \text{ mol } Al_2(SO_4)_3}\right)$ or $\left(\dfrac{1 \text{ mol } Al_2(SO_4)_3}{3 \text{ mol S}}\right)$

(c) 0.600 mol Al

(d) 3.48 mol S

4.39 0.0725 mol N_2, 0.218 mol H_2 **4.41** 0.833 mol UF_6 **4.43** 9.33×10^{23} atoms C **4.45** 3.76×10^{24} atoms **4.47** 3.01×10^{23} atoms C–12 **4.49** **(a)** 75.4 g Fe **(b)** 392 g O **(c)** 35.1 g Ca **4.51** 1.30×10^{-10} g K **4.53** 0.302 mol Ni

4.55 Note: all masses are in g/mole

(a) $NaHCO_3$	84.0066 g/mol
(b) $(NH_4)_2CO_3$	96.0858 g/mol
(c) $CuSO_4 \cdot 5H_2O$	249.685 g/mole
(d) $K_2Cr_2O_7$	294.1846 g/mole
(e) $Al_2(SO_4)_3$	342.151 g/mol

4.57 **(a)** 388 g $Ca_3(PO_4)_2$ **(b)** 0.151 g $Fe(NO_3)_3$ **(c)** 3.49×10^{-5} g C_4H_{10} **(d)** 139 g $(NH_4)_2CO_3$ **4.59** **(a)** 0.215 moles $CaCO_3$ **(b)** 9.16×10^{-11} moles NH_3 **(c)** 7.94×10^{-2} moles $Sr(NO_3)_2$ **(d)** 4.31×10^{-8} moles Na_2CrO_4 **4.61** 0.0750 moles of Ca, 3.01 g Ca **4.63** 1.30 mol N, 62.5 g $(NH_4)_2CO_3$ **4.65** 3.43 kg fertilizer

4.67 Assume one mole total for each of the following.
(a) 19.2% Na, 1.68% H, 25.8% P, 53.3% O
(b) 12.2% N, 5.26% H, 25.9% P, 55.6% O
(c) 62.0% C, 10.4% H, 27.6% O
(d) 23.3% Ca, 18.6% S, 55.7% O, 2.34% H
(e) 23.2% Ca, 18.6% S, 55.7% O, 2.34% H

4.69 Heroin has a higher percentage oxygen **4.71** Freon 141b has a higher percentage chlorine **4.73** 22.9% P, 77.1% Cl **4.75** These data are consistent with the experimental values cited in the problem. **4.77** 0.474 g O **4.79** **(a)** SCl **(b)** CH_2O **(c)** NH_3 **(d)** AsO_3 **(e)** HO **4.81** $NaTcO_4$ **4.83** CCl_2 **4.85** $C_9H_8O_2$ **4.87** C_2H_6O **4.89** $C_{19}H_{30}O_2$ **4.91** **(a)** $Na_2S_4O_6$ **(b)** $C_6H_4Cl_2$ **(c)** $C_6H_3Cl_3$ **4.93** $C_{19}H_{30}O_2$ **4.95** HgBr, Hg_2Br_2 **4.97** CHNO, $C_3H_3N_3O_3$

4.99 **(a)** 2 atoms of Ba, 20 atoms of O, and 36 atoms of H
(b) 2 moles of Ba, 20 moles of O, and 36 moles of H

4.101 $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

4.103 **(a)** $Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$
(b) $2AgNO_3 + CaCl_2 \longrightarrow Ca(NO_3)_2 + 2AgCl$
(c) $Pb(NO_3)_2 + Na_2SO_4 \longrightarrow PbSO_4 + 2NaNO_3$
(d) $2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$
(e) $2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$

4.105 **(a)** $Mg(OH)_2 + 2HBr \longrightarrow MgBr_2 + 2H_2O$
(b) $2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$
(c) $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$
(d) $2KHCO_3 + H_3PO_4 \longrightarrow K_2HPO_4 + 2H_2O + 2CO_2$
(e) $C_9H_{20} + 14O_2 \longrightarrow 9CO_2 + 10H_2O$

4.107 $4NH_2CHO + 5O_2 \longrightarrow 4CO_2 + 6H_2O + 2N_2$

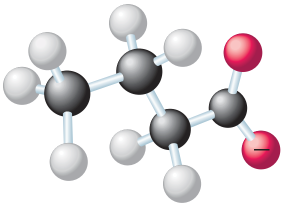
4.109 **(a)** 0.030 mol Cl_2 **(b)** 0.24 mol HCl **(c)** 0.15 mol H_2O **(d)** 0.15 mol H_2O **4.111** **(a)** 3.6 g Zn **(b)** 22 g Au **(c)** 55 g $Au(CN)_2^-$ **4.113** **(a)** $4P + 5O_2 \longrightarrow P_4O_{10}$ **(b)** 8.85 g O_2

(c) 14.2 g P_4O_{10} **(d)** 3.26 g P **4.115** 30.28 g HNO_3 **4.117** 0.47 kg O_2 **4.119** 2 molecules of SO_2 **4.121** **(a)** Fe_2O_3 is the limiting reactant **(b)** 195 g Fe **4.123** 26.7 g $FeCl_3$ **4.125** 0.913 mg HNO_3 **4.127** 66.98 g $BaSO_4$, 96.22% **4.129** 88.72% **4.131** 9.2 g C_7H_8

Chapter 5

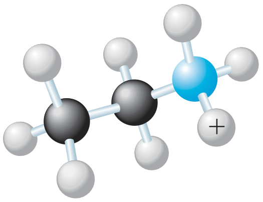
Practice Exercises

5.1 **(a)** $FeCl_3(s) \longrightarrow Fe^{3+}(aq) + 3Cl^-(aq)$
(b) $K_3PO_4(s) \longrightarrow 3K^+(aq) + PO_4^{3-}(aq)$
5.2 **(a)** $MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$
(b) $Al(NO_3)_3(s) \longrightarrow Al^{3+}(aq) + 3NO_3^-(aq)$
(c) $Na_2CO_3(s) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq)$
5.3 Molecular: $(NH_4)_2SO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaSO_4(s) + 2NH_4NO_3(aq)$
Ionic: $2NH_4^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \longrightarrow BaSO_4(s) + 2NH_4^+(aq) + 2NO_3^-(aq)$
Net ionic: $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
5.4 Molecular: $CdCl_2(aq) + Na_2S(aq) \longrightarrow CdS(s) + 2NaCl(aq)$
Ionic: $Cd^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + S^{2-}(aq) \longrightarrow CdS(s) + 2Na^+(aq) + 2Cl^-(aq)$
Net ionic: $Cd^{2+}(aq) + S^{2-}(aq) \longrightarrow CdS(s)$
5.5 $HCHO_2(aq) + H_2O \longrightarrow H_3O^+(aq) + CHO_2^-(aq)$
5.6



$CH_3CH_2CH_2CHOOH(l) + H_2O \longrightarrow CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$

5.7 $H_3C_6H_5O_7(s) + H_2O \longrightarrow H_3O^+(aq) + H_2C_6H_5O_7^-(aq)$
$H_2C_6H_5O_7^-(aq) + H_2O \longrightarrow H_3O^+(aq) + HC_6H_5O_7^{2-}(aq)$
$HC_6H_5O_7^{2-}(aq) + H_2O \longrightarrow H_3O^+(aq) + C_6H_5O_7^{3-}(aq)$
5.8 $(C_2H_5)_3N(aq) + H_2O \longrightarrow (C_2H_5)_3NH^+(aq) + OH^-(aq)$
5.9 $HONH_2(aq) + H_2O \longrightarrow HONH_3^+(aq) + OH^-(aq)$
5.10



$CH_3CH_2NH_2(aq) + H_2O \longrightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$

5.11 $CH_3NH_2(aq) + H_2O \longrightarrow CH_3NH_3^+(aq) + OH^-(aq)$
5.12 $HNO_2(aq) + H_2O \longrightarrow H_3O^+(aq) + NO_2^-(aq)$
5.13 sodium arsenate **5.14** calcium formate, calcium methanoate **5.15** hydrofluoric acid, sodium fluoride; hydrobromic acid, sodium bromide **5.16** Iodic acid **5.17** $NaHSO_3$, sodium hydrogen sulfite
5.18 $H_3PO_4(aq) + NaOH(aq) \longrightarrow NaH_2PO_4(aq) + H_2O$
sodium dihydrogen phosphate
$NaH_2PO_4(aq) + NaOH(aq) \longrightarrow Na_2HPO_4(aq) + H_2O$
sodium hydrogen phosphate
$Na_2HPO_4(aq) + NaOH(aq) \longrightarrow Na_3PO_4(aq) + H_2O$
sodium phosphate
5.19 Molecular: $Zn(NO_3)_2(aq) + Ca(C_2H_3O_2)_2(aq) \longrightarrow Zn(C_2H_3O_2)_2(aq) + Ca(NO_3)_2(aq)$
Ionic: $Zn^{2+}(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2C_2H_3O_2^-(aq) \longrightarrow Zn^{2+}(aq) + 2C_2H_3O_2^-(aq) + Ca^{2+}(aq) + 2NO_3^-(aq)$
Net ionic: No reaction
5.20 **(a)** Molecular: $AgNO_3(aq) + NH_4Cl(aq) \longrightarrow AgCl(s) + NH_4NO_3(aq)$
Ionic: $Ag^+(aq) + NO_3^-(aq) + NH_4^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) + NH_4^+(aq) + NO_3^-(aq)$
Net ionic: $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(b) Molecular: $Na_2S(aq) + Pb(C_2H_3O_2)_2(aq) \longrightarrow 2NaC_2H_3O_2(aq) + PbS(s)$
Ionic: $2Na^+(aq) + S^{2-}(aq) + Pb^{2+}(aq) + 2C_2H_3O_2^-(aq) \longrightarrow 2Na^+(aq) + 2C_2H_3O_2^-(aq) + PbS(s)$
Net ionic: $S^{2-}(aq) + Pb^{2+}(aq) \longrightarrow PbS(s)$
5.21 Molecular: $2HNO_3(aq) + Ca(OH)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O$
Ionic: $2H^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2OH^-(aq) \longrightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + 2H_2O$
Net ionic: $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
5.22 **(a)** Molecular: $HCl(aq) + KOH(aq) \longrightarrow H_2O + KCl(aq)$
Ionic: $H^+(aq) + Cl^-(aq) + K^+(aq) + OH^-(aq) \longrightarrow H_2O + K^+(aq) + Cl^-(aq)$
Net ionic: $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
(b) Molecular: $HCHO_2(aq) + LiOH(aq) \longrightarrow H_2O + LiCHO_2(aq)$
Ionic: $HCHO_2(aq) + Li^+(aq) + OH^-(aq) \longrightarrow H_2O + Li^+(aq) + CHO_2^-(aq)$
Net ionic: $HCHO_2(aq) + OH^-(aq) \longrightarrow H_2O + CHO_2^-(aq)$
(c) Molecular: $N_2H_4(aq) + HCl(aq) \longrightarrow N_2H_5Cl(aq)$
Ionic: $N_2H_4(aq) + H^+(aq) + Cl^-(aq) \longrightarrow N_2H_5^+(aq) + Cl^-(aq)$
Net ionic: $N_2H_4(aq) + H^+(aq) \longrightarrow N_2H_5^+(aq)$
5.23 Molecular: $CH_3NH_2(aq) + HCHO_2(aq) \longrightarrow CH_3NH_3CHO_2(aq)$
Ionic: $CH_3NH_2(aq) + HCHO_2(aq) \longrightarrow CH_3NH_3^+(aq) + CHO_2^-(aq)$
Net ionic: $CH_3NH_2(aq) + HCHO_2(aq) \longrightarrow CH_3NH_3^+(aq) + CHO_2^-(aq)$
5.24 Molecular: $2HCHO_2(aq) + Co(OH)_2(s) \longrightarrow Co(CHO_2)_2(aq) + 2H_2O$
Ionic: $2HCHO_2(aq) + Co(OH)_2(s) \longrightarrow 2CHO_2^-(aq) + Co^{2+}(aq) + 2H_2O$
Net ionic: $2HCHO_2(aq) + Co(OH)_2(s) \longrightarrow 2CHO_2^-(aq) + Co^{2+}(aq) + 2H_2O$
5.25 **(a)** Formic acid, a weak acid will form.
Molecular: $KCHO_2(aq) + HCl(aq) \longrightarrow KCl(aq) + HCHO_2(aq)$
Ionic: $K^+(aq) + CHO_2^-(aq) + H^+(aq) + Cl^-(aq) \longrightarrow K^+(aq) + Cl^-(aq) + HCHO_2(aq)$
Net ionic: $CHO_2^-(aq) + H^+(aq) \longrightarrow HCHO_2(aq)$
(b) Carbonic acid will form and it will further dissociate to water and carbon dioxide:
$CuCO_3(s) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O + Cu^{2+}(aq)$
Molecular: $CuCO_3(s) + 2HC_2H_3O_2(aq) \longrightarrow CO_2(g) + H_2O + Cu(C_2H_3O_2)_2(aq)$
Ionic: $CuCO_3(s) + 2HC_2H_3O_2(aq) \longrightarrow CO_2(g) + H_2O + Cu^{2+} + 2C_2H_3O_2^-(aq)$
Net ionic: $CuCO_3(s) + 2HC_2H_3O_2(aq) \longrightarrow CO_2(g) + H_2O + Cu^{2+} + 2C_2H_3O_2^-(aq)$
(c) No reaction will occur. All acetate salts and nitrate salts are soluble
(d) Insoluble nickel hydroxide will precipitate.
$Ni^{2+}(aq) + 2OH^-(aq) \longrightarrow Ni(OH)_2(s)$

Molecular: $NiCl_2(aq) + 2NaOH(aq) \longrightarrow Ni(OH)_2(s) + 2NaCl(aq)$
Ionic: $Ni^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow$
$Ni(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$
Net ionic: $Ni^{2+}(aq) + 2OH^-(aq) \longrightarrow Ni(OH)_2(s)$
5.26 $CuO(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l)$
Or
$Cu(OH)_2(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$
5.27 You want to use a metathesis reaction that produces CoS, which is insoluble, and a second product that is soluble. You may want the reactants to be soluble.
$CoCl_2(aq) + Na_2S(aq) \longrightarrow CoS(s) + 2NaCl(aq)$
5.28 1.53 M HNO_3 **5.29** 0.1837 M **5.30** 0.0438 mol HCl
5.31 143 mL of HCl **5.32** 2.11 g $Sr(NO_3)_2$ **5.33** 0.531 g $AgNO_3$
5.34 250.0 mL **5.35** 600 mL of water. **5.36** 31.6 mL H_3PO_4
5.37 26.8 mL NaOH **5.38** 0.40 M Fe^{3+}, 1.2 M Cl^-
5.39 0.750 M Na^+ **5.40** 0.0449 M $CaCl_2$ **5.41** 60.0 mL KOH
5.42 0.605 g Na_2SO_4
5.43 **(a)** 5.41×10^{-3} mol Ca^{2+}
(b) 5.41×10^{-3} mol Ca^{2+}
(c) 5.41×10^{-3} mol $CaCl_2$
(d) 0.600 g $CaCl_2$
(e) 30.0% $CaCl_2$
(f) 70.0 % $MgCl_2$
5.44 0.178 M H_2SO_4 **5.45** 0.0220 M HCl, 0.0803%

Review Problems

5.53 $HClO_4(l) + H_2O \longrightarrow H_3O^+(aq) + ClO_4^-(aq)$
5.55 $N_2H_4(aq) + H_2O \longrightarrow N_2H_5^+(aq) + OH^-(aq)$
5.57 $HNO_2(aq) + H_2O \longrightarrow H_3O^+(aq) + NO_2^-(aq)$
5.59 $H_2CO_3(aq) + H_2O \longrightarrow H_3O^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) + H_2O \longrightarrow H_3O^+(aq) + CO_3^{2-}(aq)$
5.61 Molecular: $Na_2S(aq) + Cu(NO_3)_2(aq) \longrightarrow$
$CuS(s) + 2NaNO_3(aq)$
Ionic: $2Na^+(aq) + S^{2-}(aq) + Cu^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$
$CuS(s) + 2Na^+(aq) + 2NO_3^-(aq)$
Net: $Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS(s)$
5.63 **(a)**, **(b)**, and **(d)**.
5.65
(a) Ionic: $3Fe^{2+}(aq) + 3SO_4^{2-}(aq) + 6K^+(aq) + 2PO_4^{3-}(aq) \longrightarrow$
$Fe_3(PO_4)_2(s) + 6K^+(aq) + 3SO_4^{2-}(aq)$
Net: $3Fe^{2+}(aq) + 2PO_4^{3-}(aq) \longrightarrow Fe_3(PO_4)_2(s)$
(b) Ionic: $3Ag^+(aq) + 3C_2H_3O_2^-(aq) + Al^{3+}(aq) + 3Cl^-(aq) \longrightarrow$
$3AgCl(s) + Al^{3+}(aq) + 3C_2H_3O_2^-(aq)$
Net: $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(c) Ionic: $2Cr^{3+}(aq) + 6Cl^-(aq) + 3Ba^{2+}(aq) + 6OH^-(aq) \longrightarrow$
$2Cr(OH)_3(s) + 3Ba^{2+}(aq) + 6Cl^-(aq)$
Net: $Cr^{3+}(aq) + 3OH^-(aq) \longrightarrow Cr(OH)_3(s)$
5.67 **(a)** Molecular: $Ca(OH)_2(aq) + 2HNO_3(aq) \longrightarrow$
$Ca(NO_3)_2(aq) + 2H_2O$
Ionic: $Ca^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2NO_3^-(aq) \longrightarrow$
$Ca^{2+}(aq) + 2NO_3^-(aq) + 2H_2O$
Net: $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
(b) Molecular: $Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O$
Ionic: $Al_2O_3(s) + 6H^+(aq) + 6Cl^-(aq) \longrightarrow$
$2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2O$
Net: $Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O$
(c) Molecular: $Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + 2H_2O$
Ionic: $Zn(OH)_2(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow$
$Zn^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O$
Net: $Zn(OH)_2(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O$
5.69 The electrical conductivity would decrease regularly, until one solution had neutralized the other, forming a non-electrolyte:
$Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow$
$BaSO_4(s) + 2H_2O$
Once the point of neutralization had been reached, the addition of excess sulfuric acid would cause the conductivity to increase, because sulfuric acid is a strong electrolyte itself.
5.71 **(a)** $2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2O + CO_2(g)$
(b) $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O$
5.73 These reactions have the following "driving forces":
(a) Formation of insoluble $Cr(OH)_3$
(b) Formation of water, a weak electrolyte
5.75 **(a)** Molecular: $3HNO_3(aq) + Cr(OH)_3(s) \longrightarrow$
$Cr(NO_3)_3(aq) + 3H_2O$
Ionic: $3H^+(aq) + 3NO_3^-(aq) + Cr(OH)_3(s) \longrightarrow$
$Cr^{3+}(aq) + 3NO_3^-(aq) + 3H_2O$
Net: $3H^+(aq) + Cr(OH)_3(s) \longrightarrow Cr^{3+}(aq) + 3H_2O$
(b) Molecular: $HClO_4(aq) + NaOH(aq) \longrightarrow NaClO_4(aq) + H_2O$
Ionic: $H^+(aq) + ClO_4^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow$
$Na^+(aq) + ClO_4^-(aq) + H_2O$
Net: $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
(c) Molecular: $Cu(OH)_2(s) + 2HC_2H_3O_2(aq) \longrightarrow$
$Cu(C_2H_3O_2)_2(aq) + 2H_2O$
Ionic: $Cu(OH)_2(s) + 2H^+(aq) + 2C_2H_3O_2^-(aq) \longrightarrow$
$Cu^{2+}(aq) + 2C_2H_3O_2^-(aq) + 2H_2O$
Net: $Cu(OH)_2(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + 2H_2O$
(d) Molecular: $ZnO(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2O$
Ionic: $ZnO(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow$
$Zn^{2+}(aq) + SO_4^{2-}(aq) + H_2O$
Net: $ZnO(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2O$
5.77 **(a)** Molecular: $Na_2SO_3(aq) + Ba(NO_3)_2(aq) \longrightarrow$
$BaSO_3(s) + 2NaNO_3(aq)$
Ionic: $2Na^+(aq) + SO_3^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$
$BaSO_3(s) + 2Na^+(aq) + 2NO_3^-(aq)$
Net: $Ba^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow BaSO_3(s)$
(b) Molecular: $2HCHO_2(aq) + K_2CO_3(aq) \longrightarrow$
$CO_2(g) + H_2O + 2KCHO_2(aq)$
Ionic: $2H^+(aq) + 2CHO_2^-(aq) + 2K^+(aq) + CO_3^{2-}(aq) \longrightarrow$
$CO_2(g) + H_2O + 2K^+(aq) + 2CHO_2^-(aq)$
Net: $2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O$
(c) Molecular: $2NH_4Br(aq) + Pb(C_2H_3O_2)_2(aq) \longrightarrow$
$2NH_4C_2H_3O_2(aq) + PbBr_2(s)$
Ionic: $2NH_4^+(aq) + 2Br^-(aq) + Pb^{2+}(aq) + 2C_2H_3O_2^-(aq) \longrightarrow$
$2NH_4^+(aq) + 2C_2H_3O_2^-(aq) + PbBr_2(s)$
Net: $Pb^{2+}(aq) + 2Br^-(aq) \longrightarrow PbBr_2(s)$
(d) Molecular: $2NH_4ClO_4(aq) + Cu(NO_3)_2(aq) \longrightarrow$
$Cu(ClO_4)_2(aq) + 2NH_4NO_3(aq)$
Ionic: $2NH_4^+(aq) + 2ClO_4^-(aq) + Cu^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$
$Cu^{2+}(aq) + 2ClO_4^-(aq) + 2NO_3^-(aq) + 2NH_4^+(aq)$
Net: N.R.
5.79 There are numerous possible answers. One of many possible sets of answers would be:
(a) $NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O$
(b) $FeCl_2(aq) + 2NaOH(aq) \longrightarrow Fe(OH)_2(s) + 2NaCl(aq)$
(c) $Ba(NO_3)_2(aq) + K_2SO_3(aq) \longrightarrow BaSO_3(s) + 2KNO_3(aq)$
(d) $2AgNO_3(aq) + Na_2S(aq) \longrightarrow Ag_2S(s) + 2NaNO_3(aq)$
(e) $ZnO(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2O$
5.81 **(a)** 1.00 M NaOH **(b)** 0.577 M $CaCl_2$
5.83 658 mL $NaC_2H_3O_2$
5.85 **(a)** 1.46 g NaCl **(b)** 16.2 g $C_6H_{12}O_6$ **(c)** 6.13 g H_2SO_4
5.87 0.11 M H_2SO_4 **5.89** 300 mL. **5.91** 225 mL water

5.93 **(a)** 0.0147 mol Ca^{2+}, 0.0294 mol Cl^-
(b) 0.0204 mol Al^{3+}, 0.061 mol Cl^-
5.95 **(a)** 0.25 M Cr^{2+}, 0.50 M NO_3^-
(b) 0.10 M Cu^{2+}, 0.10 M SO_4^{2-}
(c) 0.48 M Na^+, 0.16 M PO_4^{3-}
(d) 0.15 M Al^{3+}, 0.22 M SO_4^{2-}
5.97 1.07 g $Al_2(SO_4)_3$ **5.99** 11.9 mL $NiCl_2$ soln, 0.36 g $NiCO_3$
5.101 0.113 *M* KOH
$KOH(aq) + HCl(aq) \longrightarrow KCl(aq) + H_2O$
5.103 0.485 g $Al_2(SO_4)_3$ **5.105** 2.00 mL $FeCl_3$ soln, 0.129 g AgCl
5.107 13.3 mL $AlCl_3$ **5.109** 0.167 *M* Fe^{3+}, 3.67 g Fe_2O_3
5.111 0.114 *M* HCl **5.113** **(a)** 2.67×10^{-3} mol $HC_3H_5O_3$
(b) 0.240 g
5.115 **(a)** 3.56×10^{-3} mol Pb, 0.7386 g Pb, 48.40 % Pb

Chapter 6

Practice Exercises

6.1 Oxygen is reduced since it gains electrons. Sodium is oxidized since it loses electrons.

6.2 Aluminum is oxidized and is, therefore, the reducing agent. Chlorine is reduced and is, therefore, the oxidizing agent.

6.3 Fe_2O_3 is reduced and is, therefore, the oxiding agent. Al is oxidized and is, therefore, the reducing agent.

6.4 +3

6.5 **(a)** Ni +2; Cl –1
(b) Mg +2; Ti +4; O –2
(c) K +1; Cr +6; O –2
(d) H +1; P +5, O –2
(e) V +3; C 0; H +1; O –2
(f) N –3; H +1

6.6 +8/3.

6.7 **(a)** Mo +3; Cl −1
(b) Mo +4; S −2
(c) Mo +6; O −2; Cl −1
(d) Mo +6; P −3

6.8 $KClO_3 + 3HNO_2 \longrightarrow KCl + 3HNO_3$
$KClO_3$ is reduced and HNO_2 is oxidized.

6.9 There is no simple way to tell which chlorines are reduced and which are oxidized in this reaction. One analysis would have the Cl in Cl_2 end up as the Cl in NaCl, while the Cl in $NaClO_2$ ends up as the Cl in ClO_2. In this case Cl_2 is reduced and is the oxidizing agent, while $NaClO_2$ is oxidized and is the reducing agent.

6.10 The product is water, because the oxygen is reduced.

6.11 CH_4 undergoes oxidation and O_2 undergoes reduction. This means that CH_4 is the reducing agent and O_2 is the oxidizing agent.

6.12 The charges are not balanced.

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

6.13 $3Sn^{2+} + 16H^+ + 2TcO_4^- \longrightarrow 2Tc^{4+} + 8H_2O + 3Sn^{4+}$
6.14 $4Cu + 2NO_3^- + 10H^+ \longrightarrow 4Cu^{2+} + N_2O + 5H_2O$
6.15 $4C_5H_5N + 29O_2 \longrightarrow 4NO_2 + 20CO_2 + 10H_2O$
6.16 $4OH^- + SO_2 \longrightarrow SO_4^{2-} + 2e^- + 2H_2O$
6.17 $2MnO_4^- + 3C_2O_4^{2-} + 4OH^- \longrightarrow 2MnO_2 + 6CO_3^{2-} + 2H_2O$
6.18 $6Br_2 + 12OH^- \longrightarrow 10Br^- + 2BrO_3^- + 6H_2O$
6.19 $Zn + 2MnO_2 \longrightarrow ZnO + Mn_2O_3$
6.20 $Zn \longrightarrow Zn^{2+} + 2e^-$ $2H^+ + 2e^- \longrightarrow H_2$
6.21 **(a)** Molecular: $Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$
Ionic: $Mg(s) + 2H^+(aq) + 2Cl^-(aq) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq) + H_2(g)$
Net ionic: $Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$
(b) Molecular: $2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$
Ionic: $2Al(s) + 6H^+(aq) + 6Cl^-(aq) \longrightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$
Net ionic: $2Al(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2(g)$
6.22 $H_2SO_4 + 8HI \longrightarrow H_2S + 4I_2 + 4H_2O$
6.23 $Cu^{2+}(aq) + Mg(s) \longrightarrow Cu(s) + Mg^{2+}(aq)$
6.24 **(a)** $2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$
(b) $Ag(s) + Mg^{2+}(aq) \longrightarrow$ No reaction
6.25 $2C_{20}H_{42}(s) + 21O_2(g) \longrightarrow 40C(s) + 42H_2O(g)$
6.26 $2C_5H_8(g) + 9O_2(g) \longrightarrow 10CO_2(g) + 8H_2O(g)$
6.27 $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$
6.28 $2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$
6.29 $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

Review Problems

6.23 The sum of the oxidation numbers should be equal to the total charge:
(a) S^{2-}: –2
(b) SO_2: S +4, O –2
(c) P_4: P 0
(d) PH_3: P –3, H +1

6.25 The sum of the oxidation numbers should be equal to the total charge:
(a) O: −2
Na: +1
Cl: +1
(b) O: −2
Na: +1
Cl: +3
(c) O: −2
Na: +1
Cl: +5
(d) O: −2
Na: +1
Cl: +7

6.27 The sum of the oxidation numbers should be zero:
(a) S: −2
Pb: +2
(b) Cl: −1
Ti: +4
(c) Cs +1
O −1/2 (The Cs can only have an oxidation number of +1 or 0.)
(d) F −1
O +1

6.29 Ti +3; N −3 **6.31** O_3; oxidation number of O is 0

6.33 In the forward direction: **Cl_2 is reduced**. However, in HOCl, chlorine has an oxidation number of +1, so **Cl_2 also is oxidized!** (One atom is reduced, the other is oxidized.) In the reverse direction: Cl^- ion is oxidized: This means **Cl^- is the reducing agent**. **HOCl is the oxidizing agent**.

6.35 **(a)** Substance reduced (and oxidizing agent): HNO_3
Substance oxidized (and reducing agent): H_3AsO_3
(b) Substance reduced (and oxidizing agent): HOCl
Substance oxidized (and reducing agent): NaI
(c) Substance reduced (and oxidizing agent): $KMnO_4$
Substance oxidized (and reducing agent): $H_2C_2O_4$
(d) Substance reduced (and oxidizing agent): H_2SO_4
Substance oxidized (and reducing agent): Al

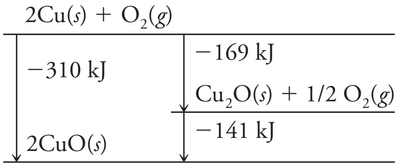
6.37 **(a)** $OCl^- + 2S_2O_3^{2-} + 2H^+ \longrightarrow S_4O_6^{2-} + Cl^- + H_2O$
(b) $2NO_3^- + Cu + 4H^+ \longrightarrow 2NO_2 + Cu^{2+} + 2H_2O$
(c) $3H_3AsO_3 + IO_3^- \longrightarrow I^- + 3H_3AsO_4$
(d) $Zn + SO_4^{2-} + 4H^+ \longrightarrow Zn^{2+} + SO_2 + 2H_2O$
(e) $NO_3^- + 4Zn + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$
(f) $2Cr^{3+} + 3BiO_3^- + 4H^+ \longrightarrow Cr_2O_7^{2-} + 3Bi^{3+} + 2H_2O$
(g) $I_2 + 5OCl^- + H_2O \longrightarrow 2IO_3^- + 5Cl^- + 2H^+$
(h) $2Mn^{2+} + 5BiO_3^- + 14H^+ \longrightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$
(i) $3H_3AsO_3 + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3H_3AsO_4 + 2Cr^{3+} + 4H_2O$

6.39 **(a)** $2CrO_4^{2-} + 3S^{2-} + 4H_2O \longrightarrow 2CrO_2^{-} + 3S + 8OH^{-}$
(b) $3C_2O_4^{2-} + 2MnO_4^{-} + 4H_2O \longrightarrow$
$6CO_2 + 2MnO_2 + 8OH^{-}$
(c) $4ClO_3^{-} + 3N_2H_4 \longrightarrow 4Cl^{-} + 6NO + 6H_2O$
(d) $NiO_2 + 2Mn(OH)_2 \longrightarrow Ni(OH)_2 + Mn_2O_3 + H_2O$
(e) $3SO_3^{2-} + 2MnO_4^{-} + H_2O \longrightarrow$
$3SO_4^{2-} + 2MnO_2 + 2OH^{-}$
6.41 $10H^{+}(aq) + NO_3^{-}(aq) + 4Mg(s) \longrightarrow$
$NH_4^{+}(aq) + 4Mg^{2+}(aq) + 3H_2O$
6.43 $4OCl^{-} + S_2O_3^{2-} + H_2O \longrightarrow 4Cl^{-} + 2SO_4^{2-} + 2H^{+}$
6.45 $O_3 + Br^{-} \longrightarrow BrO_3^{-}$
6.47 **(a)** M: $Mn(s) + 2HCl(aq) \longrightarrow MnCl_2(aq) + H_2(g)$
I: $Mn(s) + 2H^{+}(aq) + 2Cl^{-}(aq) \longrightarrow$
$Mn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$
NI: $Mn(s) + 2H^{+}(aq) \longrightarrow Mn^{2+}(aq) + H_2(g)$
(b) M: $Cd(s) + 2HCl(aq) \longrightarrow CdCl_2(aq) + H_2(g)$
I: $Cd(s) + 2H^{+}(aq) + 2Cl^{-}(aq) \longrightarrow$
$Cd^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$
NI: $Cd(s) + 2H^{+}(aq) \longrightarrow Cd^{2+}(aq) + H_2(g)$
(c) M: $Sn(s) + 2HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$
I: $Sn(s) + 2H^{+}(aq) + 2Cl^{-}(aq) \longrightarrow$
$Sn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$
NI: $Sn(s) + 2H^{+}(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$
6.49 **(a)** $3Ag(s) + 4HNO_3(aq) \longrightarrow$
$3AgNO_3(aq) + 2H_2O + NO(g)$
(b) $Ag(s) + 2HNO_3(aq) \longrightarrow AgNO_3(aq) + H_2O + NO_2(aq)$
6.51 **(a)** N.R.
(b) $2Cr(s) + 3Pb^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Pb(s)$
(c) $2Ag^{+}(aq) + Fe(s) \longrightarrow 2Ag(s) + Fe^{2+}(aq)$
(d) $3Ag(s) + Au^{3+}(aq) \longrightarrow Au(s) + 3Ag^{+}(aq)$
6.53 Increasing ease of oxidation: Pt, Ru, Tl, Pu
6.55 $Cd(s) + 2TlCl(aq) \longrightarrow CdCl_2(aq) + 2Tl(s)$
6.57 $5Mg(s) + 5Zn^{2+}(aq) + 10Cl^{-+}(aq) \longrightarrow$
$5Mg^{2+}(aq) + 10Cl^{-}(aq) + 5Zn(s)$
6.59 $10Li(s) + 10H_2O(l) \longrightarrow 5H_2(g) + 10OH^{-}(aq)$
6.61 **(a)** $2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(g)$
(b) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$
(c) $C_{21}H_{44}(s) + 32O_2(g) \longrightarrow 21CO_2(g) + 22H_2O(g)$
6.63 **(a)** $2C_6H_6(l) + 9O_2(g) \longrightarrow 12CO(g) + 6H_2O(g)$
$2C_4H_{10}(g) + 9O_2(g) \longrightarrow 8CO(g) + 10H_2O(g)$
$2C_{21}H_{44}(s) + 43O_2(g) \longrightarrow 42CO(g) + 44H_2O(g)$
(b) $2C_6H_6(l) + 3O_2(g) \longrightarrow 12C(s) + 6H_2O(g)$
$2C_4H_{10}(g) + 5O_2(g) \longrightarrow 8C(s) + 10H_2O(g)$
$C_{21}H_{44}(s) + 11O_2(g) \longrightarrow 21C(s) + 22H_2O(g)$
6.65 $2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$
6.67 $2(CH_3)_2S(g) + 9O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g) + 2SO_2(g)$
6.69 **(a)** $2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$
(b) $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$
(c) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
(d) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$
6.71 **(a)** $IO_3^{-} + 3SO_3^{2-} \longrightarrow I^{-} + 3SO_4^{2-}$
(b) 9.55 g Na_2SO_3
6.73 3.53 g Cu
6.75 **(a)** $2MnO_4^{-} + 5Sn^{2+} + 16H^{+} \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$
(b) 17.4 mL $KMnO_4$
6.77 **(a)** 6.38×10^{-3} M I_3^{-}
(b) 1.01×10^{-3} g SO_2
(c) 2.10×10^{-3}%
(d) 21 ppm
6.79 **(a)** 9.463% **(b)** 18.40%
6.81 **(a)** 0.02994 g H_2O_2 **(b)** 2.994% H_2O_2
6.83 **(a)** $2CrO_4^{2-} + 3SO_3^{2-} + H_2O \longrightarrow$
$2CrO_2^{-} + 3SO_4^{2-} + 2OH^{-}$
(b) 0.875 g Cr in the original alloy
(c) 25.4% Cr
6.85 **(a)** 5.405×10^{-3} mol $C_2O_4^{2-}$ **(b)** 0.5999 g $CaCl_2$
(c) 24.35% $CaCl_2$

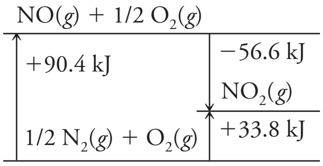
Chapter 7

Practice Exercises

7.1 55.1 J/°C **7.2** 5335 J, 5.34 kJ, 1275 cal, 1.28 kcal
7.3 127. 3 °C
7.4 12.4 kJ $°C^{-1}$ **7.5** 394 kJ/mol carbon **7.6** −58 kJ mol^{-1} NaOH
7.7 3.7 kJ, 74 kJ/mole **7.8** 24.3 kJ/mole
7.9 $\frac{1}{4}CH_4(g) + \frac{1}{2}O_2(g) \longrightarrow \frac{1}{4}CO_2(g) + \frac{1}{2}H_2O(l)$
$\Delta H = -222.6$ kJ
7.10 $5H_2(g) + 2.5O_2(g) \longrightarrow 5H_2O(l) \quad \Delta H = -1429.5$ kJ
7.11



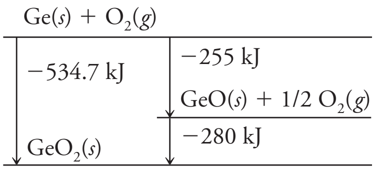
7.12



7.13 +857.7 kJ **7.14** +99.2 kJ **7.15** −44.0 kJ **7.16** 385 kJ
7.17 2.62×10^{6} kJ
7.18 $\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s)$
7.19 $Na(s) + \frac{1}{2}H_2(g) + C(s) + \frac{3}{2}O_2(g) \longrightarrow NaHCO_3(s)$
7.20 −10.98 kJ
7.21 $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g) \qquad \Delta H_f^\circ = -395.2$ kJ/mol
$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H_f^\circ = -296.9$ kJ/mol
Reverse the first reaction and add the two reactions together to get
$SO_3(g) \longrightarrow SO_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H_f^\circ = +98.3$ kJ
The answers for the enthalpy of reaction are the same using either method.
7.22 **(a)** −113.1 kJ **(b)** −177.8 kJ

Review Problems

7.40 −17 J **7.42** +100 J **7.44** 250 J **7.46** −1320 J, −315 cal
7.48 45.7 g H_2O **7.50** **(a)** 1.67×10^{3} J **(b)** 1.67×10^{3} J
(c) 23.2 J $°C^{-1}$ **(d)** 4.64 J g^{-1} $°C^{-1}$ **7.52** 25.12 J mol^{-1} $°C^{-1}$
7.54 −30.4 kJ **7.56** $HNO_3(aq) + KOH(aq) \longrightarrow$
$KNO_3(aq) + H_2O$, 3800 J, −53 kJ mol^{-1}
7.58 **(a)** $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O$
(b) 2.22×10^{5} J, **(c)** – 222 kJ/mol
7.60 **(a)** $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H^\circ = -566$ kJ,
(b) –283 kJ/mol
7.62 162 kJ of heat are evolved
7.64 8.64 g
7.66



7.68 $2NO_2(g) \longrightarrow N_2O_4(g) \quad \Delta H° = -57.93\text{ kJ}$
$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H° = -113.14\text{ kJ}$
$2NO(g) + O_2(g) \longrightarrow N_2O_4(g) \quad \Delta H° = -171.07\text{ kJ}$

7.70 $\frac{1}{2}\,Na_2O(s) + HCl(g) \longrightarrow \frac{1}{2}\,H_2O(l) + NaCl(s)$
$\Delta H° = -253.66\text{ kJ}$
$NaNO_2(s) \longrightarrow \frac{1}{2}\,Na_2O(s) + \frac{1}{2}\,NO_2(g) + \frac{1}{2}\,NO(g)$
$\Delta H° = +213.57\text{ kJ}$
$\frac{1}{2}\,NO(g) + \frac{1}{2}\,NO_2(g) \longrightarrow \frac{1}{2}\,N_2O(g) + \frac{1}{2}\,O_2(g)$
$\Delta H° = -21.34\text{ kJ}$
$\frac{1}{2}\,H_2O(l) + \frac{1}{2}\,O_2(g) + \frac{1}{2}\,N_2O(g) \longrightarrow HNO_2(l)$
$\Delta H° = -17.18\text{ kJ}$
$HCl(g) + NaNO_2(s) \longrightarrow HNO_2(l) + NaCl(s)$
$\Delta H° = -78.61\text{ kJ}$

7.72 $\frac{1}{2}\,CaO(s) + \frac{1}{2}\,Cl_2(g) \longrightarrow \frac{1}{2}\,CaOCl_2(s) \quad \Delta H° = \frac{1}{2}\,(-110.9\text{ kJ})$
$\frac{1}{2}\,H_2O(l) + \frac{1}{2}\,CaOCl_2(s) + NaBr(s) \longrightarrow$
$NaCl(s) + \frac{1}{2}\,Ca(OH)_2(s) + \frac{1}{2}\,Br_2(l) \quad \Delta H° = \frac{1}{2}\,(-60.2\text{ kJ})$
$\frac{1}{2}\,Ca(OH)_2(s) \longrightarrow \frac{1}{2}\,CaO(s) + \frac{1}{2}\,H_2O(l) \quad \Delta H° = \frac{1}{2}\,(+65.1\text{ kJ})$
$\frac{1}{2}\,Cl_2(g) + NaBr(s) \longrightarrow NaCl(s) + \frac{1}{2}\,Br_2(l)$
$\Delta H° = \frac{1}{2}\,(-106\text{ kJ}) = -53\text{ kJ}$

7.74 $12NH_3(g) + 21O_2(g) \longrightarrow 12NO_2(g) + 18H_2O(g)$
$\Delta H° = 3(-1132\text{ kJ})$
$12NO_2(g) + 16NH_3(g) \longrightarrow 14N_2(g) + 24H_2O(g)$
$\Delta H° = 2(-2740\text{ kJ})$
$28NH_3(g) + 21O_2(g) \longrightarrow 14N_2(g) + 42H_2O(g)$
$\Delta H° = -8876\text{ kJ}$
$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$
$\Delta H° = 1/7(-8876\text{ kJ}) = -1268\text{ kJ}$

7.76 Only **(c)** satisfies this requirement

7.78 **(a)** $2C(s, \text{graphite}) + 2H_2(g) + O_2(g) \longrightarrow HC_2H_3O_2(l)$
$\Delta H_f° = -487.0\text{ kJ}$
(b) $2C(s, \text{graphite}) + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow C_2H_5OH(l)$
$\Delta H_f° = -277.63\text{ kJ}$
(c) $Ca(s) + \frac{1}{8}S_8(s) + 3O_2(g) + 2H_2(g) \longrightarrow CaSO_4 \cdot 2H_2O(s)$
$\Delta H_f° = -2021.1\text{ kJ}$
(d) $2Na(s) + \frac{1}{8}S_8(s) + 2O_2(g) \longrightarrow Na_2SO_4(s)$
$\Delta H_f° = -1384.5\text{ kJ}$

7.80 **(a)** −196.6 kJ **(b)** −177.8 kJ

7.82 $C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$
$\Delta H_f° = -2.21 \times 10^3\text{ kJ}$

Chapter 8

Practice Exercises

8.1 5.10×10^{14} Hz **8.2** 2.75×10^{13} Hz **8.3** 3.25 m
8.4 2.63 μm
8.5 656 nm, which is red
8.6 **(a)** 4, 2
(b) 5, 3
(c) 7, 0
Each value of ℓ has a corresponding letter.

8.7 When $n = 2$, ℓ can be 0, or 1. Thus we have *s*, and *p* subshells. When $n = 5$, ℓ can be 0, 1, 2, 3, or 4. Thus we have *s*, *p*, *d*, *f*, and *g* subshells.
Shell 1: 1 subshell
Shell 2: 2 subshells
Shell 3: 3 subshells
Shell 4: 4 subshells
Shell 5: 5 subshells
Shell 6: 6 subshells

8.8 **(a)** Mg: $1s^22s^22p^63s^2$
(b) Ge: $1s^22s^22p^63s^23p^63d^{10}4s^24p^2$
(c) Cd: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$
(d) Gd: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^75s^25p^65d^16s^2$

8.9 The electron configuration of an element follows the periodic table. The electrons are filled in the order of the periodic table and the energy levels are determined by the row the element is in and the subshell is given by the column, the first two columns are the *s*-block, the last six columns are the *p*-block, the *d*-block has ten columns, and the *f*-block has 14 columns.

8.10 **(a)** O: $1s^22s^22p^4$
S: $1s^22s^22p^63s^23p^4$
Se: $1s^22s^22p^63s^23p^63d^{10}4s^24p^4$
(b) P: $1s^22s^22p^63s^23p^3$
N: $1s^22s^22p^3$
Sb: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3$
The elements have the same number of electrons in the valence shell, and the only differences between the valence shells are the energy levels.

8.11 **(a)**
Na: ⇅ ⇅ ⇅⇅⇅ ↑
1*s* 2*s* 2*p* 3*s*

(b)
S: ⇅ ⇅ ⇅⇅⇅ ⇅ ⇅↑↑
1*s* 2*s* 2*p* 3*s* 3*p*

(c)
Fe: ⇅ ⇅ ⇅⇅⇅ ⇅ ⇅⇅⇅ ⇅ ⇅↑↑↑↑
1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d*

8.12 **(a)** 0 unpaired electrons **(b)** 2 unpaired electrons **(c)** 0 unpaired electrons **(d)** 8 unpaired electrons
8.13 Yes
8.14 **(a)**
P: [Ne]$3s^23p^3$
[Ne] ⇅ ↑↑↑
3*s* 3*p*
(3 unpaired electrons)

(b)
Sn: [Kr]$4d^{10}5s^25p^2$
[Kr] ⇅⇅⇅⇅⇅ ⇅ ↑↑○
4*d* 5*s* 5*p*
(2 unpaired electrons)

8.15 Based on the definition of valence, there are no examples where more than 8 electrons would occupy the valence shell. For representative elements the valence shell is defined as the occupied shell with the highest value of *n*. In the ground state atom, only *s* and *p* electrons fit this definition. The transition elements have outer electron configurations: $(n\text{-}1)d^{n}\ ns^{m}$ so the valence shell is the *ns* subshell.

8.16 **(a)** Se: $4s^24p^4$ **(b)** Sn: $5s^25p^2$ **(c)** I: $5s^25p^5$
8.17 **(a)** Sn **(b)** Ga **(c)** Cr **(d)** S^{2-}
8.18 **(a)** P **(b)** Fe^{3+} **(c)** Fe **(d)** Cl^-
8.19 **(a)** Be **(b)** C **8.20** **(a)** C^{2+} **(b)** Mg^{2+}

Review Problems

8.73 6.88×10^{14} Hz
8.75 4.38×10^{13} Hz
8.77 1.02×10^{15} Hz
8.79 2.965 m
8.81 5.00×10^6 m, 5.00×10^3 km
8.83 2.7×10^{-19} J photon^{-1}, 1.6×10^5 J mol^{-1}
8.85 **(a)** Violet (see Figure 8.7) **(b)** 7.307×10^{14} s^{-1} **(c)** 4.842×10^{-19} J

8.87 1094 nm We would not expect to see the light since it is not in the visible region **8.89** 1.737×10^{-6} m, We would not expect to see the light since it is not in the visible region.

8.91 (a) *p* **(b)** *f*

8.93 (a) $n = 3, \ell = 0$ **(b)** $n = 5, \ell = 2$

8.95 0, 1, 2, 3, 4, 5

8.97 (a) $m_\ell = 1, 0,$ or -1 **(b)** $m_\ell = 3, 2, 1, 0, -1, -2,$ or -3

8.99 When $m_\ell = -4$ the minimum value of ℓ is 4 and the minimum value of n is 5.

8.101

n	ℓ	m_ℓ	m_s
2	1	−1	+1/2
2	1	−1	−1/2
2	1	0	+1/2
2	1	0	−1/2
2	1	+1	+1/2
2	1	+1	−1/2

8.103 21 electrons have $\ell = 1$, 20 electrons have $\ell = 2$

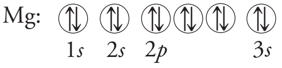
8.105 (a) S $1s^22s^22p^63s^23p^4$
(b) K $1s^22s^22p^63s^23p^64s^1$
(c) Ti $1s^22s^22p^63s^23p^63d^24s^2$
(d) Sn $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$

8.107 (a) Mn is paramagnetic **(b)** As is paramagnetic **(c)** S is paramagnetic **(d)** Sr is not paramagnetic **(e)** Ar is not paramagnetic

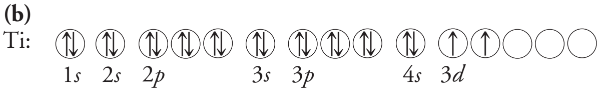
8.109 (a) Mg, zero unpaired electrons **(b)** P, three unpaired electrons **(c)** V, three unpaired electrons

8.111 (a) Ni $[Ar]3d^84s^2$ **(b)** Cs $[Xe]6s^1$ **(c)** Ge $[Ar]\ 3d^{10}4s^24p^2$ **(d)** Br $[Ar]\ 3d^{10}4s^24p^5$ **(e)** Bi $[Xe]\ 4f^{14}5d^{10}6s^26p^3$

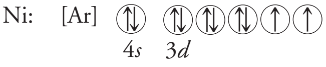
8.113 (a)



(b)



8.115 (a)



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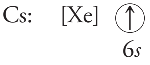

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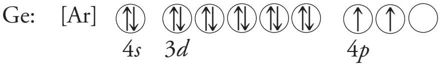

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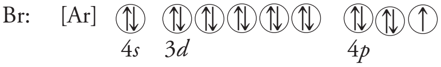
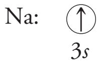


8.117 (a) 5 **(b)** 4 **(c)** 4 **(d)** 6

8.119 (a) Na $3s^1$ **(b)** Al $3s^23p^1$ **(c)** Ge $4s^24p^2$ **(d)** P $3s^23p^3$

8.121 (a)



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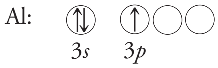

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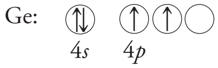

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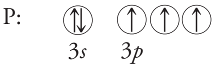


8.123 (a) 1 **(b)** 6 **(c)** 7 **8.125 (a)** Mg **(b)** Bi **8.127** Sb **8.129 (a)** Na **(b)** Co^{2+} **(c)** Cl^- **8.131 (a)** N **(b)** S **(c)** Cl **8.133 (a)** Br **(b)** As **8.135** Mg

Chapter 9

Practice Exercises

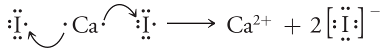
9.1 There is one electron missing, and it should go into the 5*s* orbital, and the 5*p* orbital should be empty.

$1s^12s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$

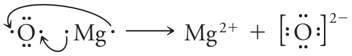
9.2 (a) Cr^{2+}: $[Ar]3d^4$ The 4*s* electron and one 3*d* electron are lost.
(b) Cr^{3+}: $[Ar]3d^3$ The 4*s* electron and two 3*d* electrons are lost.
(c) Cr^{6+}: [Ar] The 4*s* electron and all of the 3*d* electrons are lost.

9.3 The electron configurations are identical

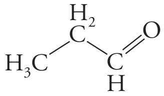
9.4



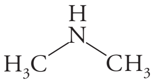
9.5



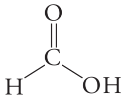
9.6



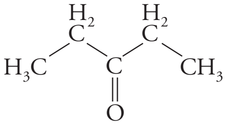
aldedyde



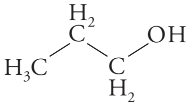
amine



acid

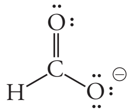


ketone



alcohol

9.7 (a) CH_3NHCH_3
(b) HCOOH
(c)



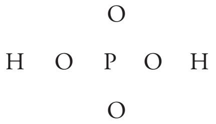
9.8 1.24 D

9.9 0.795 e^-

9.10 The bond is polar and the Cl carries the negative charge.

9.11 (a) Br **(b)** Cl **(c)** Cl

9.12

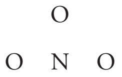


$$\begin{array}{ccccc} & & O & & \\ H & O & P & O & H \\ & & O & & \end{array}$$

32 valence electrons

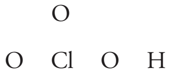
9.13 SO_2 O S O

NO_3^-



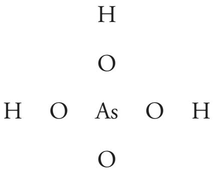
$$\begin{array}{ccc} & O & \\ O & N & O \end{array}$$

$HClO_3$



$$\begin{array}{cccc} & O & & \\ O & Cl & O & H \end{array}$$

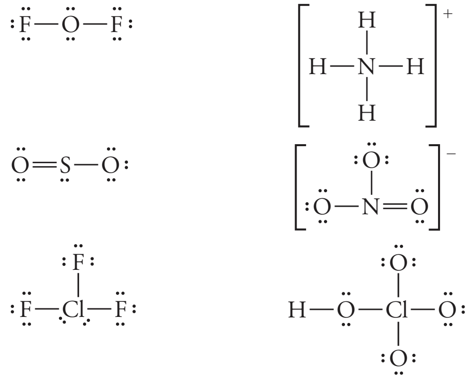
H_3AsO_4



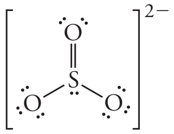
$$\begin{array}{ccccc} & & H & & \\ & & O & & \\ H & O & As & O & H \\ & & O & & \end{array}$$

9.14 SO_2 has 18 valence electrons
SeO_4^{2-} has 32 valence electrons
NO^+ has 10 valence electrons

9.15

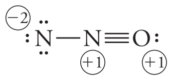


9.16 The negative sign should be on the oxygen atoms.

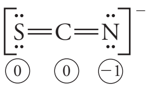


9.17

(a)

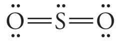


(b)



9.18

(a)



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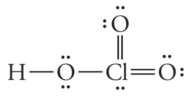

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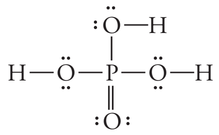
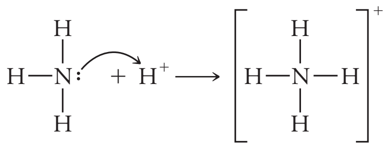
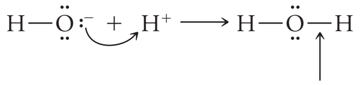


9.19

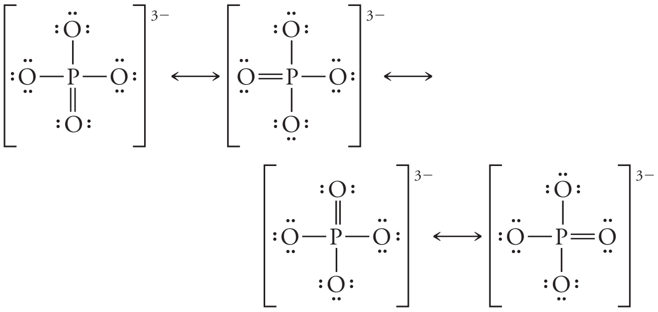


There is no difference between the coordinate covalent bond and the other covalent bonds.

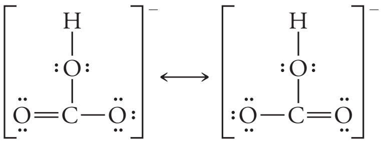
9.20



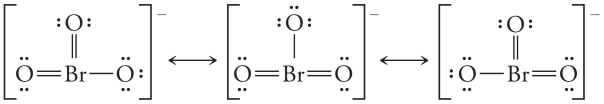
9.21



9.22



9.23



Review Problems

9.60 In order for $NaCl_2$ to be more stable than NaCl, the lattice energy should be almost 30 times larger. 4.36×10^3 kJ/148 kJ = 29.5

9.62 Magnesium loses two electrons and bromine gains an electron. To keep the overall change of the formula unit neutral, two Br^- ions combine with one Mg^{2+} ion to form $MgBr_2$.

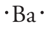
9.64 [Xe] $4f^{14}5d^{10}6s^2$, [Xe]$4f^{14}5d^{10}$

9.66 [Ar]$3d^4$ 4 unpaired electrons

9.68 **(a)**

(b)

(c)



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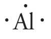
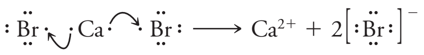


(e)

9.70

(a)



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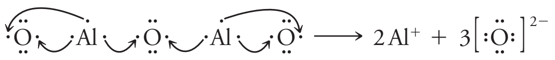

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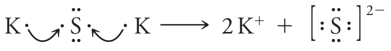
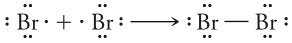


9.72 0.029 e^-, The nitrogen atom is positive.

9.74 0.42 e^-

9.76 4.029×10^{-19} J/molecule

9.78 344 nm, ultraviolet region

9.80 (a)


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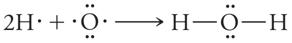

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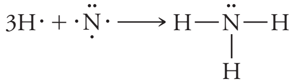
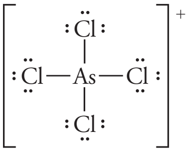


9.82 (a) H_2Se **(b)** H_3As **(c)** SiH_4

9.84 (a) S **(b)** Si **(c)** Br **(d)** C

9.86 N—S

9.88

(a)


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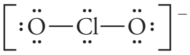

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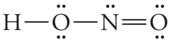

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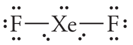

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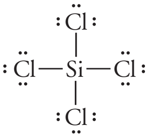

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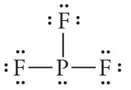

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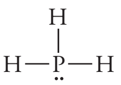

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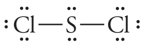
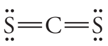


9.92 (a)


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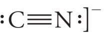

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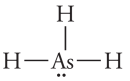

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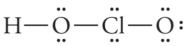

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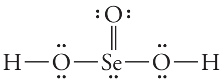
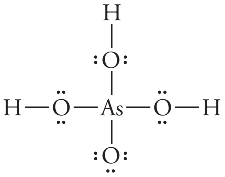


(d)


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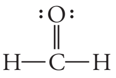

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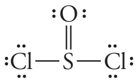

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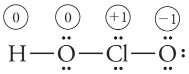
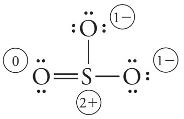
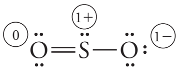
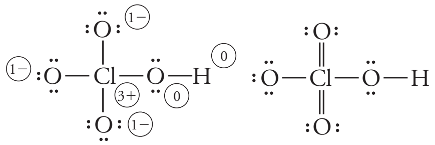
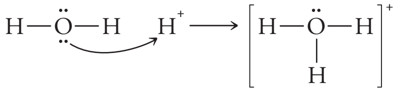


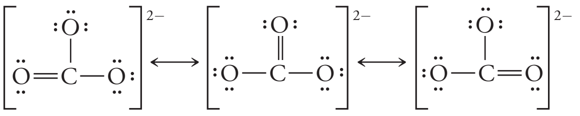
(b)


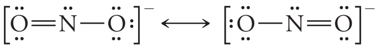
(c)


9.100


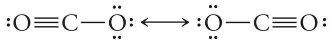
9.102 The formal charges on all of the atoms of the left structure are zero, therefore, the potential energy of this molecule is lower and it is more stable. Group 2 atoms normally have only two bonds.

9.104


9.106 The average bond order is 4/3


9.108


N—O bonds in NO_2^- should be shorter than that in NO_3^-.

9.110


These are not preferred structures, because in each Lewis diagram, one oxygen bears a formal charge of +1 whereas the other bears a formal charge of –1.

Chapter 10

Practice Exercises

10.1 Octahedral

10.2 Trigonal bipyramidal

10.3 Linear

10.4 Linear

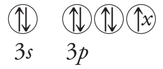
10.5 Square planar

10.6 In SO_3^{2-} trigonal pyramidal
$PbCl_4$ tetrahedral
XeO_4 tetrahedral
OF_2 bent

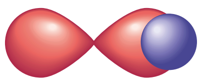
10.7 Polar

10.8 (a) Non-polar. **(b)** polar. **(c)** polar. **(d)** polar. **(e)** polar.

10.9 The H–Cl bond is formed by the overlap of the half-filled 1*s* atomic orbital of a H atom with the half-filled 3*p* valence orbital of a Cl atom:

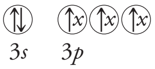
Cl atom in HCl (x = H electron):


The overlap that gives rise to the H–Cl bond is that of a 1*s* orbital of H with a 3*p* orbital of Cl:

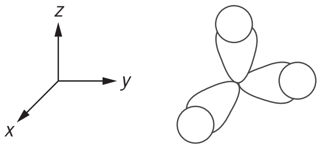


10.10 The half-filled 1*s* atomic orbital of each H atom overlaps with a half-filled 3*p* atomic orbital of the P atom, to give three P–H

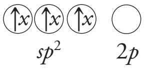
bonds. This should give a bond angle of 90°.
P atom in PH_3 (x = H electron):



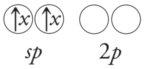
The orbital overlap that forms the P–H bond combines a 1*s* orbital of hydrogen with a 3*p* orbital of phosphorus. (Note: only half of each p orbital is shown):



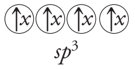
10.11 sp^2 hybrid orbitals on the B, x = Cl electron



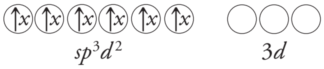
10.12 *sp* hybrid orbitals on the Be; x = F electron



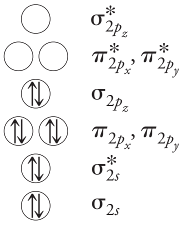
10.13 sp^3



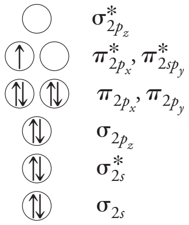
10.14 Since there are five bonding pairs of electrons on the central phosphorous atom, we choose sp^3d hybridization for the P atom. Each of phosphorous's five sp^3d hybrid orbitals overlaps with a 3*p* atomic orbital of a chlorine atom to form a total of five P–Cl single bonds. Four of the 3*d* atomic orbitals of P remain unhybridized.
10.15 Trigonal bipyramidal, sp^3d—*p* bonds
10.16 sp^3d^2
10.17 **(a)** sp^3 **(b)** sp^3d
10.18 NH_3 is sp^3 hybridized. Three of the electron pairs are used for bonding with the three hydrogens. The fourth pair of electrons is a lone pair of electrons. This pair of electrons is used for the formation of the bond between the nitrogen of NH_3 and the hydrogen ion, H^+.
10.19 Octahderal, sp^3d^2
P atom in PCl_6^- (x = Cl electron):



10.20 Atom 1: sp^2 atom 2: sp^3 atom 3: sp^2
There are 10 σ bonds and 2 π bonds in the molecule.
10.21 Atom 1: *sp* atom 2: sp^2 atom 3: sp^3
There are 9 σ bonds and 3 π bonds in the molecule.
10.22 The bond order is 3 and this does agree with the Lewis structure.



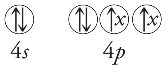
10.23



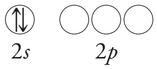
The bond order is 5/2

Review Problems

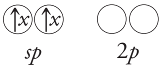
10.76 **(a)** Bent
(b) Planar triangular
(c) T-shaped
(d) Linear
(e) Planar triangular
10.78 **(a)** Nonlinear
(b) Trigonal bipyramidal
(c) Trigonal pyramidal
(d) Trigonal pyramidal
(e) Nonlinear
10.80 **(a)** Tetrahedral
(b) Square planar
(c) Octahedral
(d) Tetrahedral
(e) Linear
10.82 BrF_4^+
10.84 180°
10.86 **(a)** 109.5° **(b)** 109.5°
(c) 120° **(d)** 180°
(e) 109.5°
10.88 **(a)**, **(b)**, and **(c)**
10.90 All are polar
10.92 In SF_6, although the individual bonds in this substance are polar bonds, the geometry of the bonds is symmetrical which serves to cause the individual dipole moments of the various bonds to cancel one another. In SF_5Br, one of the six bonds has a different polarity so the individual dipole moments of the various bonds do not cancel one another.
10.94 The 1*s* atomic orbitals of the hydrogen atoms overlap with the mutually perpendicular *p* atomic orbitals of the selenium atom.
Se atom in H_2Se (x = H electrons):



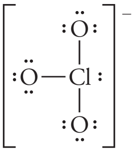
10.96 Atomic Be:



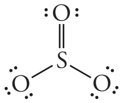
Hybridized Be: (x = a Cl electron)



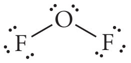
10.98 **(a)** sp^3



(b) sp^2

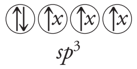


(c) sp^3



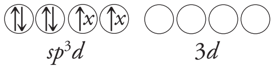
10.100 (a) sp^3

The hybrid orbital diagram for As: (x = a Cl electron)

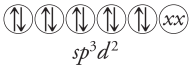


(b) sp^3d

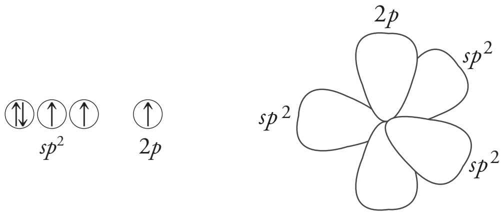
The hybrid orbital diagram for Cl: (x = a F electron)

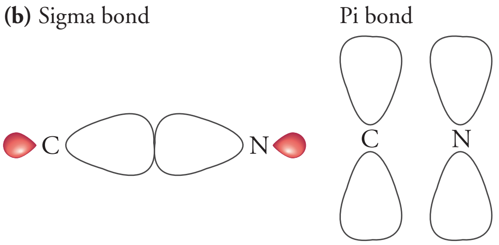


10.102 Sb in SbF_6^-: (xx = an electron pair from the donor F^-)

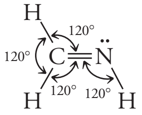


10.104 (a) N in the C═N system:





(c)



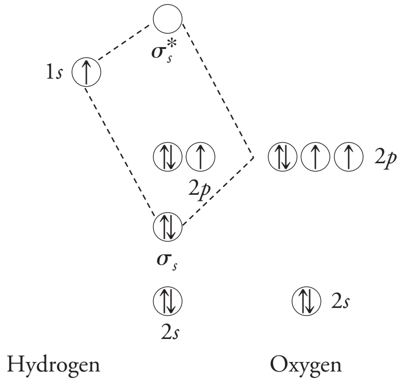
10.106 Each carbon atom is sp^2 hybridized, and each C—Cl bond is formed by the overlap of an sp^2 hybrid of carbon with a p atomic orbital of a chlorine atom. The C═C double bond consists first of a C—C σ bond formed by "head on" overlap of sp^2 hybrids from each C atom. Second, the C═C double bond consists of a side-to-side overlap of unhybridized p orbitals of each C atom, to give one π bond. The molecule is planar, and the expected bond angles are all 120°.

10.108 1. sp^3 **2.** sp **3.** sp^2 **4.** sp^2

10.110 (a) O_2^+ **(b)** O_2 **(c)** N_2

10.112 (a) N_2^+ **(b)** NO **(c)** O_2^-

10.114



There are two electrons in bonding MOs and three electrons in nonbonding MOs.
The bond order is 1.

Chapter 11

Practice Exercises

11.1 14.1 psi, 28.7 in. Hg
11.2 88,800 pascal, 666 torr
11.3 1270 mm Hg, 270 mm Hg
11.4 653 mm Hg
11.5 2/3
11.6 750 torr
11.7 688 torr
11.8 9.00 L O_2
11.9 64.6 L air
11.10

$$V_{O_2} = \left(\frac{1 \text{ volume } O_2}{2 \text{ volume NO}}\right) \times 184 \text{ ml NO} = 92 \text{ mL } O_2$$

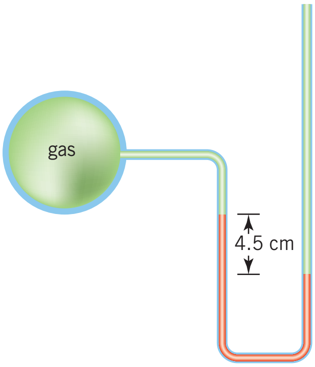
$$V_2 = \frac{(723 \text{ torr})(92.0 \text{ mL})(295 \text{ K})}{(755 \text{ torr})(318 \text{ K})} = 81.7 \text{ mL } O_2$$

11.11 15,000 g solid CO_2
11.12 1,130 g Ar
11.13 58.1 g/mol
11.14 132 g mol^{-1}, Xe
11.15 Since radon is almost eight times denser than air, the sensor should be in the lowest point in the house: the basement.
11.16 2.77 g/L
11.17 P_2F_4
11.18 114 g mol^{-1}
9 C and 6 H
8 C and 18 H
7 C and 30 H
6 C and 42 H
5 C and 54 H
4 C and 66 H
3 C and 78 H
2 C and 90 H
1 C and 102 H
The most probable compound is C_8H_{18}
11.19 3.07 L CO_2, 6.14 L SO_2, total volume = 9.21 L
11.20 1.03 g $CaCO_3$
11.21 $P_{Ar} = 6.80$ atm, $P_{N_2} = 9.34$ atm, $P_{O_2} = 11.04$ atm, $P_{total} = 27.18$ atm
11.22 2713 g O_2
11.23 746 torr, 0.0994 mol CH_4
11.24 732 torr, 289 mL
11.25 1.125 atm
11.26 $P_{H_2} = 0.996$ atm
$P_{NO} = 1.05$ atm
11.27 0.147, 14.7%
11.28 0.988
11.29 HI

Review Problems

11.25 (a) 958 torr **(b)** 0.974 atm **(c)** 738 mm Hg **(d)** 10.9 torr
11.27 (a) 250 torr **(b)** 350 torr

11.29 4.5 cm Hg



11.31 813 torr
11.33 125 torr
11.35 507 mL
11.37 4.37 L
11.39 843 °C
11.41 801 torr
11.43 5.69 L
11.45 −53 °C
11.47 $6.24 \times 10^4 \frac{\text{mL torr}}{\text{mol K}}$
11.49 0.104 L
11.51 2340 torr
11.53 0.0398 g
11.55 **(a)** $1.34\ g\ L^{-1}$ **(b)** $1.25\ g\ L^{-1}$ **(c)** $3.17\ g\ L^{-1}$ **(d)** $1.78\ g\ L^{-1}$
11.57 1.28 g/L
11.59 88.2 g/mol
11.61 1.14×10^3 mL
11.63 10.7 L H_2
11.65 36.3 mL O_2
11.67 224 mL
11.69 697 torr
11.71
$P_{N_2} = 0.30$ atm, $P_{O_2} = 0.20$ atm, $P_{He} = 0.40$ atm, $P_{CO_2} = 0.10$ atm
$P_{N_2} = 228$ torr, $P_{O_2} = 152$ torr, $P_{He} = 304$ torr, $P_{CO_2} = 76$ torr
$P_{N_2} = 0.304$ bar, $P_{O_2} = 0.203$ bar, $P_{He} = 0.405$ bar, $P_{CO_2} = 0.101$ bar
11.73 734 torr, 262 mL
11.75 250 mL
11.77 N_2, 1.25
11.79 $^{235}UF_6$, 1.0043

Chapter 12

Practice Exercises

12.1 **(a)** $CH_3CH_2CH_2CH_2CH_3 < CH_3CH_2OH < KBr$
(b) $CH_3CH_2OCH_2CH_3 < CH_3CH_2NH_2 < HOCH_2CH_2CH_2CH_2OH$
12.2 Propylamine, because of its ability to form hydrogen bonds
12.3 The piston should be pushed in.
12.4 The number of molecules in the vapor will decrease, and the number of molecules in the liquid will increase, but the sum of the molecules in the vapor and the liquid remains the same.
12.5 Decreasing the temperature will decrease the vapor pressure and, therefore, decrease the number of molecules in the vapor state. The volume will remain constant as long as the external pressure on the piston is also decreased by the same amount as the product of nT.
12.6 The boiling point is most likely **(a)** less than 10 °C above 100 °C.
12.7 Approximately 75 °C
12.8 3.0×10^4 J
12.9 The heat released when 10 g of water vapor condenses is 2.7×10^4 J.
The heat content of 10 g of water at 100 °C cooling to 37 °C is 2.6×10^3 J.
12.10 530 mm Hg
12.11 350.5 K
12.12 Adding heat will shift the equilibrium to the right, producing more vapor.
12.13

Boiling	Endothermic
Melting	Endothermic
Condensing	Exothermic
Subliming	Endothermic
Freezing	Exothermic

No, each physical change is always exothermic or always endothermic as shown.
12.14 Vapor pressure curve. See Figure 12.23
12.15 Solid to gas
12.16 Liquid
12.17 2 Cr atoms
12.18 The ratio is 1 to 1.
12.19 A molecular crystal
12.20 A covalent or network solid.
12.21 A molecular solid

Review Problems

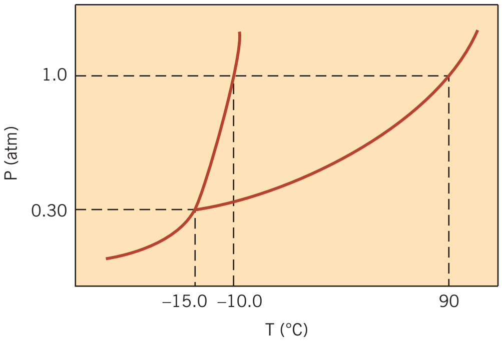
12.83 Diethyl ether
12.85 **(a)** London forces, dipole–dipole and hydrogen bonding
(b) London forces, dipole–dipole
(c) London forces
(d) London forces, dipole–dipole
12.87 Chloroform would be expected to display larger dipole-dipole attractions because it has a larger dipole moment than bromoform. On the other hand, bromoform would be expected to show stronger London forces due to having larger electron clouds, which are more polarizable than those of chlorine.

Since bromoform in fact has a higher boiling point that chloroform, we must conclude that it experiences stronger intermolecular attractions than chloroform, which can only be due to London forces. Therefore, London forces are more important in determining the boiling points of these two compounds.
12.89 London forces are higher in chains than in branched isomers. Therefore, octane has higher London forces between molecules than 2,2,3,3-tetramethylbutane so octane would be more viscous.
12.91 Ethanol
12.93 Ether < acetone < benzene < water < acetic acid
12.95

Compound	Intermolecular forces broken
CH_3CH_2OH	London, dipole, hydrogen bonding
H_3CCN	London, dipole
NaCl	London, Ionic

12.97 305 kJ
12.99 **(a)** The final temperature will be 0 °C.
(b) 47.9 g of water must melt.
12.101 3.46×10^{-6} atm
12.103 $31{,}400\ J\ mol^{-1}$

12.105



12.107 **(a)** Solid **(b)** gas **(c)** liquid **(d)** solid, liquid, and gas
12.109 4 Zn^{2+}, 4 S^{2-}
12.111 3.51 Å, 351 pm
12.113 656 pm
12.115 **(a)** 6.57° **(b)** 27.3°
12.117 176 pm
12.119 Molecular solid
12.121 Metallic solid
12.123 **(a)** molecular **(d)** metallic **(g)** ionic
(b) ionic **(e)** covalent
(c) ionic **(f)** molecular

Chapter 13

Practice Exercises

13.1 3.7 g L^{-1}, Hydrogen sulfide is more soluble in water than nitrogen and oxygen. Hydrogen sulfide reacts with the water to form hydronium ions and HS^-.
13.2 1.12 mg O_2, 1.85 mg N_2 mL
13.3 405.7 mL water
13.4 0.250 g of NaBr, 24.75 g H_2O, 25.0 mL H_2O
13.5 2.0×10^1 g
13.6 1.239 *m*, smaller
13.7 g CH_3OH for 0.050 m = 0.320 g
g CH_3OH for 0.100 m = 0.640 g
g CH_3OH for 0.150 m = 0.960 g
g CH_3OH for 0.200 m = 1.28 g
g CH_3OH for 0.250 m = 1.60 g
13.8 **(a)** 28.3 g **(b)** 70.7 g **(c)** 1.41 g
13.9 27 *m*
13.10 16.1 *m*
13.11 6.82 *M*
13.12 0.00469 *M*, $Al(NO_3)_3$, 0.00470 *m* $Al(NO_3)_3$
13.13 4.90×10^2 torr
13.14 34.5 g stearic acid
13.15 55.4 torr
13.16 45.1 torr
13.17 89.5% to 91.2%
13.18 213 g glucose
13.19 157 g mol^{-1}
13.20 125 g mol^{-1}
13.21 3.68 mm Hg, 50.0 mm H_2O
13.22 222 torr, B. P. = 100.006 °C, M. P. = −0.021 °C note that the significant figure rules were not used for the boiling points
13.23 5.00×10^3 g mol^{-1}
13.24 5.38×10^2 g mol^{-1}
13.25 −0.882 °C, −0.441 °C
13.26 **(a)** −0.372 °C **(b)** −0.0372 °C **(c)** −0.00372 °C

The first freezing point depression, solution **(a)**, could be estimated using a laboratory thermometer that can measure 1 °C increments.

Review Problems

13.42 $KCl(s) \longrightarrow K^+(g) + Cl^-(g)$, $\Delta H° = +715\ kJ\ mol^{-1}$
$K^+(g) + Cl^-(g) \longrightarrow K^+(aq) + Cl^-(aq)$, $\Delta H° = -686\ kJ\ mol^{-1}$
$KCl(s) \longrightarrow K^+(aq) + Cl^-(aq)$, $\Delta H° = +29\ kJ\ mol^{-1}$
13.44 0.038 g/L
13.46 0.020 g L^{-1}
13.48 3.35 *m*
13.50 0.133 *m*, 2.39×10^{-3}, 2.34%
13.52 5.45%
13.54 7.89%, 4.76 *m*
13.56 0.359 *M* $NaNO_3$, 3.00 %, 6.49×10^{-3}
13.58 22.8 torr
13.60 52.7 torr
13.62 70 mol% toluene and 30 mol% benzene
13.64 **(a)** 0.029 **(b)** 2.99×10^{-2} moles **(c)** 278 g/mol
13.66 68.9 g
13.68 240 g/mol
13.70 127 g/mol, $C_8H_4N_2$.
13.72 **(a)** If the equation is correct, the units on both sides of the equation should be g/mol. The units on the right side of this equation are:

$$\frac{(g) \times (\cancel{L}\ \cancel{atm}\ mol^{-1}\ \cancel{K^{-1}}) \times (\cancel{K})}{\cancel{L} \times \cancel{atm}} = g/mol$$

which is correct.
(b) 1.8×10^6 g/mol
13.74 15.3 torr
13.76 1.3×10^4 torr
13.78 −1.1 °C
13.80 2
13.82 1.89

Chapter 14

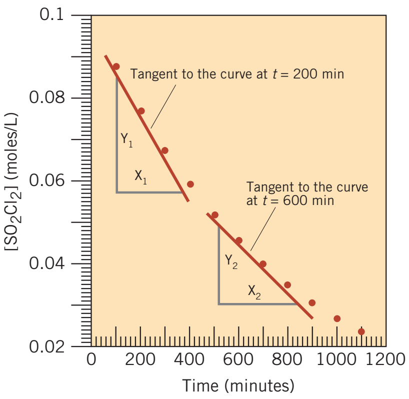
Practice Exercises

14.1 Rate of production of $I^- = 8.0 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$. Rate of production of $SO_4^{2-} = 2.4 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$.
14.2 Rate of disappearance of $O_2 = 0.45\ mol\ L^{-1}\ s^{-1}$. Rate of disappearance of $H_2S = 0.30\ mol\ L^{-1}\ s^{-1}$.
14.3 $-2.1 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$
14.4 A value near $1 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$ is correct.
14.5 **(a)** $9.8 \times 10^{14}\ L^2\ mol^{-2}\ s^{-1}$ **(b)** $L^2\ mol^{-2}\ s^{-1}$
14.6 **(a)** $8.0 \times 10^{-2}\ L\ mol^{-1}\ s^{-1}$ **(b)** $L\ mol^{-1}\ s^{-1}$
14.7 Order of the reaction with respect to $[BrO_3^-] = 1$
Order of the reaction with respect to $[SO_3^{2-}] = 1$
Overall order of the reaction = 1 + 1 = 2
14.8 Rate = $k[Cl_2]^2[NO]$
14.9 The order with respect to Br_2 is 1, the order with respect to HCO_2H is zero. The overall order of the reaction is 1.
14.10 $2.0 \times 10^2\ L^2\ mol^{-2}\ s^{-1}$. Each of the other data sets also gives the same value.
14.11 **(a)** The rate will increase nine-fold.
(b) The rate will increase three-fold.
(c) The rate will decrease by three fourths.
14.12 **(a)** Rate = $k[NO]^2[H_2]^1$
(b) $2.1 \times 10^5\ L^2\ mol^{-2}\ s^{-1}$
(c) $L^2\ mol^{-2}\ s^{-1}$

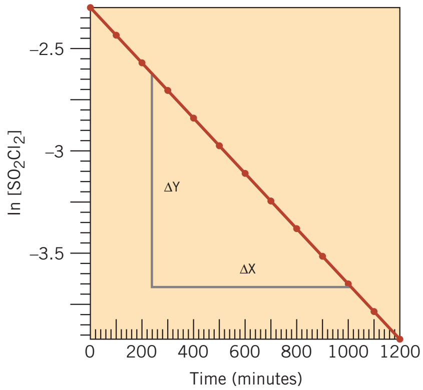
14.13 **(a)** First order with respect to sucrose
(b) $6.17 \times 10^{-4}\ \mathrm{s}^{-1}$
14.14 **(a)** Rate $= k[\mathrm{A}]^2[\mathrm{B}]^2$ **(b)** $6.9 \times 10^{-3}\ \mathrm{L}^3\ \mathrm{mol}^{-3}\ \mathrm{s}^{-1}$
(c) $\mathrm{L}^3\ \mathrm{mol}^{-3}\ \mathrm{s}^{-1}$ **(d)** 4
14.15 $2.56 \times 10^{-2}\ \mathrm{yr}^{-1}$
14.16 **(a)** $4.71 \times 10^{-3}\ M$ **(b)** 7.8 min
14.17 18.7 min, 37.4 min
14.18 27.1 yr
14.19 5.41%
14.20 1.90×10^4 yrs
14.21 The upper limit of dates is 24,800 years and the lower limit of dates is 424 years.
14.22 63 min
14.23 $4.0 \times 10^{-4}\ M$
14.24 $\mathrm{k} = 1.03\ \mathrm{L\ mol}^{-1}\ \mathrm{s}^{-1}$ $t_{1/2} = 1.48 \times 10^3\ \mathrm{s}$
14.25 The reaction is first-order
14.26 322 K or 49 °C
14.27 **(a)** 1.4×10^2 kJ/mol **(b)** $0.40\ \mathrm{L\ mol}^{-1}\ \mathrm{s}^{-1}$
14.28 684 K
14.29 **(a)**, **(b)**, and **(e)** may be elementary processes.
Equations **(c)**, **(d)**, and **(f)** are not elementary processes because they have more than two molecules colliding at one time, and this is very unlikely.
14.30 Rate $= k[\mathrm{NO}][\mathrm{O}_3]$
14.31 Rate $= \dfrac{\mathrm{k}[\mathrm{NO_2Cl}]^2}{[\mathrm{NO}_2]}$

Review Problems

14.46



At 200 min: $1 \times 10^{-4}\ M$/min. At 600 min: $7 \times 10^{-5}\ M$/min.
14.48 The rate of disappearance of hydrogen is three times the rate of disappearance of nitrogen. $\mathrm{NH_3}$ appears twice as fast as $\mathrm{N_2}$ disappears.
14.50 **(a)** Rate for $\mathrm{O_2} = 11.4\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$
(b) Rate for $\mathrm{CO_2} = 7.20\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$
(c) Rate for $\mathrm{H_2O} = 8.40\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$
14.52 **(a)** $-\dfrac{d}{dt}[\mathrm{CH_3Cl}] = -\dfrac{1}{3}\dfrac{d}{dt}[\mathrm{Cl_2}] = \dfrac{d}{dt}[\mathrm{CCl_4}] = \dfrac{1}{3}\dfrac{d}{dt}[\mathrm{HCl}]$
(b) $9.7 \times 10^{-3}\ \mathrm{M\ s}^{-1}$
14.54 $8.0 \times 10^{-11}\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$
14.56 $2.4 \times 10^2\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$
14.58 $6.4 \times 10^2\ \mathrm{M\ s}^{-1}$
14.60 Rate $= k[\mathrm{M}][\mathrm{N}]^2$, $2.5 \times 10^3\ \mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$
14.62 Rate $= k[\mathrm{OCl}^-][\mathrm{I}^-]$, $6.8 \times 10^9\ \mathrm{L\ mol}^{-1}\ \mathrm{s}^{-1}$
14.64 Rate $= k[\mathrm{ICl}][\mathrm{H_2}]$, $1.04 \times 10^{-1}\ \mathrm{L\ mol}^{-1}\ \mathrm{s}^{-1}$
14.66



$1.32 \times 10^{-3}\ \mathrm{min}^{-1}$
47.68 **(a)** $3.7 \times 10^{-3}\ M$ **(b)** $6.0 \times 10^{-4}\ M$
47.70 $1.85 \times 10^{-2}\ \mathrm{min}^{-1}$
14.72 $4.26 \times 10^{-3}\ \mathrm{min}^{-1}$
14.74 1.3×10^4 min
14.76 11 mg/kg
14.78 1/256
14.80 Approximately 500 min. The reaction is first-order in $\mathrm{SO_2Cl_2}$.
14.82 33.2 hr
14.84 1.3×10^9 years old
14.86 4.0×10^{-13}
14.88 The slope is: -9.5×10^3 K , $E_a = 79$ kJ/mol
Using the equation $E_a = 79.3$ kJ/mol
14.90 $E_a = 99$ kJ/mol, $A = 6.6 \times 10^9\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, $k = 7.9 \times 10^{-2}\ \mathrm{L\ mol}^{-1}\ \mathrm{s}^{-1}$
14.92 **(a)** $3.8 \times 10^{-5}\ \mathrm{s}^{-1}$ **(b)** $1.6 \times 10^1\ \mathrm{s}^{-1}$
14.94 Rate $= k\,[AB][C]$
14.96 The intermediate in this reaction is $\mathrm{N_2O_2}$
The overall reaction is:
$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$
Rate $= k[\mathrm{NO}]^2[\mathrm{O_2}]$

Chapter 15

Practice Exercises

15.1 $2\mathrm{N_2O_3} + \mathrm{O_2} \rightleftharpoons 4\mathrm{NO_2}$
15.2

(a) $\dfrac{[\mathrm{H_2O}]^2}{[\mathrm{H_2}]^2[\mathrm{O_2}]} = K_c$ **(b)** $\dfrac{[\mathrm{CO_2}][\mathrm{H_2O}]^2}{[\mathrm{CH_4}][\mathrm{O_2}]^2} = K_c$

15.3 1.2×10^{-13}
15.4 1.9×10^5
15.5 $K_P = \dfrac{(P_{\mathrm{N_2O}})^2}{(P_{\mathrm{N_2}})^2(P_{\mathrm{O_2}})}$
15.6 $K_P = \dfrac{(P_{\mathrm{HI}})^2}{(P_{\mathrm{H_2}})^2(P_{\mathrm{I_2}})}$
15.7 1.8×10^{36}
15.8 K_p is smaller than K_c. $K_c = 57$
15.9 $K_c = \dfrac{1}{[\mathrm{NH_3}(g)][\mathrm{HCl}(g)]}$
15.10
(a) $K_c = \dfrac{1}{[\mathrm{Cl_2}(g)]}$
(b) $K_c = [\mathrm{Na}^+(aq)][\mathrm{OH}^-(aq)][\mathrm{H_2}(g)]$

(c) $K_c = [Ag^+]^2[CrO_4^{2-}]$

(d) $K_c = \dfrac{[Ca^{+2}(aq)][HCO_3^-(aq)]^2}{[CO_2(aq)]}$

15.11 The reaction will move to the left.

15.12 (a), **(c)**, **(b)**

15.13 There will be no change in the amount of H_3PO_4.

15.14 (a) Decreasing the concentration of Cl_2 at equilibrium, the value of K_p will be unchanged.

(b) Increasing the amount of Cl_2 at equilibrium, the value of K_p will be unchanged.

(c) Increasing the amount of Cl_2 at equilibrium, decreasing the value of K_p.

(d) Decreasing the concentration of Cl_2 at equilibrium, the value of K_p will be unchanged.

15.15 [CO] decreases by 0.060 mol/L and $[CO_2]$ increases by 0.060 mol/L

15.16 $K_c = 4.06$

15.17 (a) $[PCl_3] = 0.200\ M$
$[Cl_2] = 0.100\ M$
$[PCl_5] = 0.000\ M$

(b) The change in concentration of PCl_3 was (0.200 – 0.120) $M = 0.080$ mol/L. The Cl_2 has decreased by 0.080 M and PCl_5 has increased by 0.080 M.

(c) $[PCl_3] = 0.120\ M$, $[PCl_5] = 0.080\ M$, $[Cl_2] = 0.020\ M$.

(d) $K_c = 33$

15.18 $[NO_2] = 1.04 \times 10^{-2}\ M$

15.19 $[C_2H_5OH] = 8.98 \times 10^{-3}\ M$

15.20 $[H_2] = [I_2] = 0.044\ M$, $[HI] = 0.312\ M$.

15.21 $[H_2] = 0.107\ M$
$[I_2] = 0.0066\ M$
$[HI] = 0.1868\ M$.

15.22 $[N_2] = 6.2 \times 10^{-4}$
$[H_2] = 1.9 \times 10^{-3}$

15.23 $[NO] = 1.1 \times 10^{-17}\ M$

Review Problems

15.19 (a) $K_c = \dfrac{[POCl_3]^2}{[PCl_3]^2[O_2]}$

(b) $K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

(c) $K_c = \dfrac{[NO]^2[H_2O]^2}{[N_2H_4][O_2]^2}$

(d) $K_c = \dfrac{[NO_2]^2[H_2O]^8}{[N_2H_4][H_2O_2]^6}$

(e) $K_c = \dfrac{[SO_2][HCl]^2}{[SOCl_2][H_2O]}$

15.21 (a) $K_p = \dfrac{(P_{POCl_3})^2}{(P_{PCl_3})^2(P_{O_2})}$

(b) $K_p = \dfrac{(P_{SO_2})^2(P_{O_2})}{(P_{SO_3})^2}$

(c) $K_p = \dfrac{(P_{NO})^2(P_{H_2O})^2}{(P_{N_2H_4})(P_{O_2})^2}$

(d) $K_p = \dfrac{(P_{NO_2})^2(P_{H_2O})^8}{(P_{N_2H_4})(P_{H_2O_2})^6}$

(e) $K_p = \dfrac{(P_{SO_2})(P_{HCl})^2}{(P_{SOCl_2})(P_{H_2O})}$

15.23 (a) $K_c = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$ **(b)** $K_c = \dfrac{[Cd(SCN)_4^{2-}]}{[Cd^{2+}][SCN^-]^4}$

15.25 1×10^{85}

15.27

(a) $K_c = \dfrac{[HCl]^2}{[H_2][Cl_2]}$ **(b)** $K_c = \dfrac{[HCl]}{[H_2]^{1/2}[Cl_2]^{1/2}}$

K_c for reaction (b) is the square root of K_c for reaction (a).

15.29 0.0375 M

15.31 b

15.33 $K_c = 11$

15.35 $K_p = 2.7 \times 10^{-2}$

15.37 $K_p = 5.4 \times 10^{-5}$

15.39 (a) 55.5 M **(b)** 55.5 M **(c)** 55.5 M

15.41

(a) $K_c = \dfrac{[CO]^2}{[O_2]}$

(b) $K_c = [H_2O][SO_2]$

(c) $K_c = \dfrac{[CH_4][CO_2]}{[H_2O]^2}$

(d) $K_c = \dfrac{[H_2O][CO_2]}{[HF]^2}$

(e) $K_c = [H_2O]^5$

15.43

$[HI] = 1.47 \times 10^{-12}\ M$
$[Cl_2] = 7.37 \times 10^{-13}\ M$

15.45 (a) The system shifts to the right to consume some of the added methane.

(b) The system shifts to the left to consume some of the added hydrogen.

(c) The system shifts to the right to make some more carbon disulfide.

(d) The system shifts to the left to decrease the amount of gaseous moles.

(e) The system shifts to the right to absorb some of the added heat.

15.47 (a) Right **(b)** left **(c)** left **(d)** right **(e)** no effect **(f)** left

15.49 (a) No **(b)** To the left

15.51 $[CH_3OH] = 4.36 \times 10^{-3}\ M$.

15.53 $K_c = 0.398$

15.55 $K_c = 0.0955$

15.57 $K_c = 0.915$

15.59 $[Br_2] = [Cl_2] = 0.011\ M$

15.61 $[NO_2] = [SO_2] = 0.0497$ mol/L
$[NO] = [SO_3] = 0.0703$ mol/L

15.63 $[H_2] = [CO_2] = 7.7 \times 10^{-3}\ M$
$[CO] = [H_2O] = 0.0123\ M$

15.65 $[H_2] = [Cl_2] = 8.9 \times 10^{-19}\ M$

15.67 $[CO] = 5.0 \times 10^{-4}\ M$

15.69 $[PCl_5] = 3.0 \times 10^{-5}\ M$.

15.71 $[NO_2] = [SO_2] = 0.0281\ M$

15.73 $[CO] = [H_2O] = 0.200\ M$

Chapter 16

Practice Exercises

16.1 Conjugate acid base pairs **(a)**, **(c)**, and **(f)**

(b) The conjugate base of HI is I^-

(d) The conjugate base of HNO_2 is NO_2^- and the conjugate base of NH_4^+ is NH_3

(e) The conjugate acid of CO_3^{2-} is HCO_3^- and the conjugate acid of CN^- is HCN

16.2 In each case the conjugate base is obtained by removing a proton from the acid:

(a) OH^- **(b)** I^- **(c)** NO_2^- **(d)** $H_2PO_4^-$
(e) HPO_4^{2-} **(f)** PO_4^{3-} **(g)** HS^- **(h)** NH_3

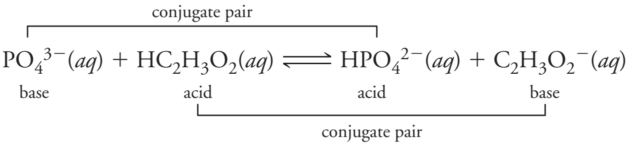
16.3 In each case the conjugate acid is obtained by adding a proton to the base:

(a) H_2O_2 **(b)** HSO_4^- **(c)** HCO_3^- **(d)** HCN
(e) NH_3 **(f)** NH_4^+ **(g)** H_3PO_4 **(h)** $H_2PO_4^-$

16.4 HCN and CN^- HCl and Cl^-

16.5 The Brønsted acids: $H_2PO_4^-(aq)$ and $H_2CO_3(aq)$
The Brønsted bases: $HCO_3^-(aq)$ and $HPO_4^{2-}(aq)$

16.6



$$PO_4^{3-}(aq) + HC_2H_3O_2(aq) \rightleftharpoons HPO_4^{2-}(aq) + C_2H_3O_2^-(aq)$$

conjugate pair
base
acid
acid
base
conjugate pair

16.7 **(a)** $H_2PO_4^-$ amphoteric, since it can both accept and donate a proton **(b)** HPO_4^{2-} amphoteric, since it can both accept and donate a proton **(c)** H_2S amphoteric, since it can both accept and donate a proton **(d)** H_3PO_4 not amphoteric: it can only donate protons **(e)** NH_4^+ not amphoteric: it can only donate protons **(f)** H_2O amphoteric, since it can both accept and donate a proton **(g)** HI not amphoteric: it can only donate protons **(h)** HNO_2 not amphoteric: it can only donate protons

16.8 $HPO_4^{2-}(aq) + OH^-(aq) \longrightarrow PO_4^{3-}(aq) + H_2O$; HPO_4^{2-} acting as an acid

$HPO_4^{2-}(aq) + H_3O^+(aq) \longrightarrow H_2PO_4^- + H_2O$; HPO_4^{2-} acting as a base

16.9 $HSO_4^-(aq) + HPO_4^{2-}(aq) \longrightarrow SO_4^{-2}(aq) + H_2PO_4^-(aq)$

16.10 The substances on the right because they are the weaker acid and base.

16.11 **(a)** $HF < HBr < HI$
(b) $PH_3 < H_2S < HCl$
(c) $H_2O < H_2Se < H_2Te$
(d) $AsH_3 < H_2Se < HBr$
(e) $PH_3 < H_2Se < HI$

16.12 **(a)** HBr **(b)** H_2Te **(c)** H_2S

16.13 **(a)** $HClO_3$ **(b)** H_2SO_4

16.14 **(a)** H_3AsO_4 **(b)** H_2TeO_4

16.15 **(a)** HIO_4 **(b)** H_2TeO_4 **(c)** H_3AsO_4

16.16 **(a)** H_2SO_4 **(b)** H_3AsO_4

16.17 The acid strength decreases as follows:
$FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

16.18 **(a)** NH_3, Lewis base
H^+, Lewis acid
(b) O^{2-}, Lewis base
SeO_3, Lewis acid
(c) Ag^+, Lewis acid
NH_3, Lewis base

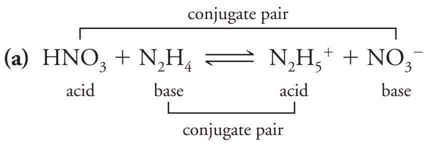
16.19 **(a)** Fluoride ions have a filled octet of electrons and are likely to behave as Lewis bases, i.e., electron pair donors.

(b) $BeCl_2$ is a likely Lewis acid since it has an incomplete shell. The Be atom has only two valence electrons and it can easily accept a pair of electrons.

(c) It could reasonably be considered a potential Lewis base since it contains three oxygens, each with lone pairs and partial negative charges. However, it is more effective as a Lewis acid, since the central sulfur bears a significant positive charge.

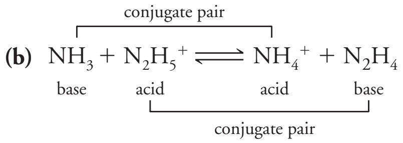
Review Problems

16.38



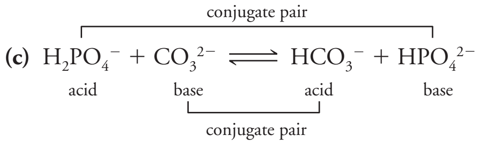
$$\text{(a)}\ HNO_3 + N_2H_4 \rightleftharpoons N_2H_5^+ + NO_3^-$$

conjugate pair
acid
base
acid
base
conjugate pair



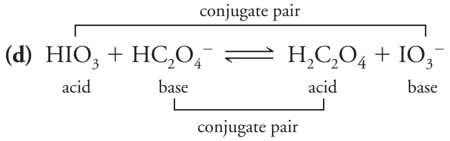
$$\text{(b)}\ NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$$

conjugate pair
base
acid
acid
base
conjugate pair



$$\text{(c)}\ H_2PO_4^- + CO_3^{2-} \rightleftharpoons HCO_3^- + HPO_4^{2-}$$

conjugate pair
acid
base
acid
base
conjugate pair



$$\text{(d)}\ HIO_3 + HC_2O_4^- \rightleftharpoons H_2C_2O_4 + IO_3^-$$

conjugate pair
acid
base
acid
base
conjugate pair

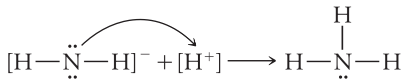
16.40 **(a)** HBr **(b)** HF **(c)** HBr

16.42 **(a)** $HClO_2$ **(b)** H_2SeO_4

16.44 **(a)** $HClO_3$ **(b)** $HClO_3$ **(c)** $HBrO_4$

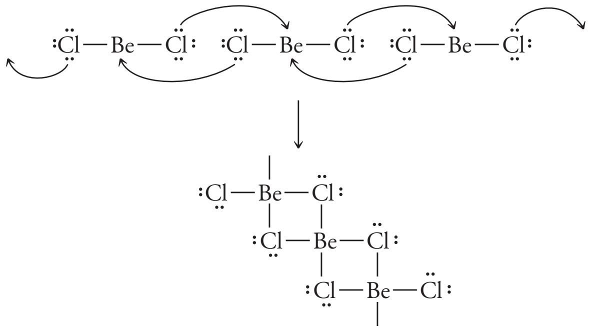
16.46 $Cr(H_2O)_6^{3+}(aq) + H_2O \longrightarrow Cr(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$

16.48

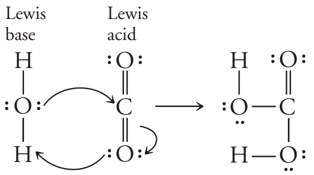


Lewis bases: NH_2^- Lewis acid: H^+

16.50

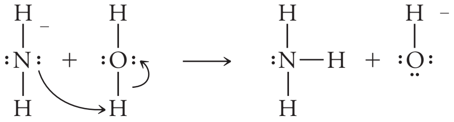


16.52



Lewis base
Lewis acid

16.54



Lewis bases: NH_2^- and OH^- Lewis acid: H^+

Chapter 17

Practice Exercises

17.1 $[OH^-] = 8.3 \times 10^{-16}\ M$

17.2 $[H_3O^+] = 1.3 \times 10^{-9}$ The solution is basic

17.3 pOH = 9.75
$[H^+] = 5.6 \times 10^{-5}\ M$
$[OH^-] = 1.8 \times 10^{-10}\ M$

17.4 pH = 4.49
pOH = 9.51

17.5 (a) $[H^+] = 1.3 \times 10^{-3}\ M$
$[OH^-] = 7.7 \times 10^{-12}\ M$
The solution is acidic.
(b) $[H^+] = 1.4 \times 10^{-4}\ M$
$[OH^-] = 7.1 \times 10^{-11}\ M$
The solution is acidic.
(c) $[H^+] = 1.6 \times 10^{-11}\ M$
$[OH^-] = 6.5 \times 10^{-4}\ M$
The solution is basic.
(d) $[H^+] = 7.8 \times 10^{-5}\ M$
$[OH^-] = 1.3 \times 10^{-10}\ M$
The solution is acidic.
(e) $[H^+] = 2.5 \times 10^{-12}\ M$
$[OH^-] = 4.1 \times 10^{-3}\ M$
The solution is basic.

17.6 $[H^+] = 0.0050\ M$
pH = 2.30
pOH =11.70

17.7 pOH = 1.07
pH = 12.93
$[H^+] = 1.2 \times 10^{-13}\ M$

17.8 $[H^+] = 3.2 \times 10^{-6}\ M$

17.9 (a) $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

(b) $(CH_3)_3NH^+ + H_2O \rightleftharpoons H_3O^+ + (CH_3)_3N$

$$K_a = \frac{[H_3O^+][(CH_3)_3N]}{[(CH_3)_3NH^+]}$$

(c) $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

17.10 (a) $HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]}$$

(b) $(CH_3)_2NH_2^+ + H_2O \rightleftharpoons H_3O^+ + (CH_3)_2NH$

$$K_a = \frac{[H_3O^+][(CH_3)_2NH]}{[(CH_3)_2NH_2^+]}$$

(c) $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

$$K_a = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

17.11 Barbituric acid and hydrazoic acid.

17.12 HA is the strongest acid. $K_a(HA) = 6.9 \times 10^{-4}$
$K_a(HB) = 7.2 \times 10^{-5}$

17.13 (a) $(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

(b) $SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$

$$K_b = \frac{[HSO_3^-][OH^-]}{[SO_3^{2-}]}$$

(c) $NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$

$$K_b = \frac{[NH_3OH^+][OH^-]}{[NH_2OH]}$$

17.14 (a) $HS^- + H_2O \rightleftharpoons H_2S + OH^-$

$$K_b = \frac{[H_2S][OH^-]}{[HS^-]}$$

(b) $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$

$$K_b = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}$$

(c) $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$

$$K_b = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]}$$

(d) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$

(e) $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$

$$K_b = \frac{[H_2SO_3][OH^-]}{[HSO_3^-]}$$

17.15 $K_b = 4.3 \times 10^{-4}$

17.16 $K_a = 1.8 \times 10^{-4}$

17.17 $K_a = 1.2 \times 10^{-3}$
$pK_a = 2.93$

17.18 $K_a = 1.7 \times 10^{-5}$
$pK_a = 4.78$

17.19 $K_b = 1.6 \times 10^{-6}$
$pK_b = 5.79$

17.20 $[H^+] = 1.2 \times 10^{-3}\ M$
pH = 2.91

17.21 $[H^+] = 8.4 \times 10^{-4}\ M$
pH = 3.08

17.22 pOH = 5.51

17.23 pH = 8.62

17.24 pH = 5.35

17.25 (a) Basic **(b)** neutral **(c)** acidic

17.26 (a) Neutral **(b)** basic **(c)** acidic

17.27 5.39

17.28 8.17

17.29 5.13

17.30 Acidic

17.31 Acidic

17.32 Upon addition of a strong acid, the concentration of $HC_2H_3O_2$ will increase. When a strong base is added, it reacts with the acid to form more of the acetate ion; therefore the concentration of the acetic acid will decrease.

17.33 (a) $H^+ + NH_3 \longrightarrow NH_4^+$
(b) $OH^- + NH_4^+ \longrightarrow H_2O + NH_3$

17.34 4.83, the difference is due to rounding errors

17.35 4.61

17.36 Acetic acid buffer, 26.2 g $NaC_2H_3O_2$
Hydrazoic acid buffer, 29.0 NaN_3
Butanoic acid buffer, 29.6 g $NaC_4H_7O_2$
Propanoic acid, 22.3 g $NaC_3H_5O_2$

17.37 Yes, 0.70, 9.66 g $NaCHO_2$

17.38 0.14 pH units

17.39 pH = 9.76, pH = 9.67

17.40

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ $\quad K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$ $\quad K_a = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$ $\quad K_a = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

17.41 $[H^+] = 2.8 \times 10^{-3}$ *M*, pH = 2.55, $[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}$

17.42 pH = 11.66, It is not a substitute for $NaHCO_3$

17.43 pH = 10.25

17.44 $[H_2SO_3] = K_{b2}$ for SO_3^{2-}

17.45

(a) H_2O, K^+, $HC_2H_3O_2$, H^+, $C_2H_3O_2^-$, and OH^-

$[H_2O] > [K^+] > [C_2H_3O_2^-] > [OH^-] > [HC_2H_3O_2] > [H^+]$

(b) H_2O, $HC_2H_3O_2$, H^+, $C_2H_3O_2^-$, and OH^-

$[H_2O] > [HC_2H_3O_2] > [H^+] = [C_2H_3O_2^-] > [OH^-]$

(c) H_2O, K^+, $HC_2H_3O_2$, H^+, $C_2H_3O_2^-$, and OH^-

$[H_2O] > [K^+] > [OH^-] > [C_2H_3O_2^-] > [HC_2H_3O_2] > [H^+]$

(d) H_2O, K^+, $HC_2H_3O_2$, H^+, $C_2H_3O_2^-$, and OH^-

$[H_2O] > [K^+] > [HC_2H_3O_2] > [H^+] > [C_2H_3O_2^-] > [OH^-]$

17.46 (a) 2.37 **(b)** 3.74 **(c)** 4.22 **(d)** 8.22

17.47 pH = 3.66

Review Problems

17.40 $[D^+] = 3.0 \times 10^{-8}\ M = [OD^-]$

pD = 7.52

pOD = 7.52

17.42 (a) $[H^+] = 1.5 \times 10^{-12}$ *M*, pH = 11.83, pOH = 2.17

(b) $[H^+] = 1.6 \times 10^{-10}$ *M*, pH = 9.81, pOH = 4.19

(c) $[H^+] = 6.3 \times 10^{-7}$ *M*, pH = 6.20, pOH = 7.80

(d) $[H^+] = 1.2 \times 10^{-3}$ *M*, pH = 2.91, pOH = 11.09

17.44 4.72

17.46 (a) $[H^+] = 7.2 \times 10^{-9}\ M$

$[OH^-] = 1.4 \times 10^{-6}\ M$

(b) $[H^+] = 2.7 \times 10^{-3}\ M$

$[OH^-] = 3.6 \times 10^{-12}\ M$

(c) $[H^+] = 5.6 \times 10^{-12}\ M$

$[OH^-] = 1.8 \times 10^{-3}\ M$

(d) $[H^+] = 5.3 \times 10^{-14}\ M$

$[OH^-] = 1.9 \times 10^{-1}\ M$

(e) $[H^+] = 2.0 \times 10^{-7}\ M$

$[OH^-] = 5.0 \times 10^{-8}\ M$

17.48 $[H^+] = 2 \times 10^{-6}\ M$

$[OH^-] = 5 \times 10^{-9}\ M$

17.50 $[H^+] = 0.00065\ M$

pH = 3.19

$[OH^-] = 1.55 \times 10^{-11}\ M$

17.52 $[OH^-] = 0.15$ *M*, pOH = 0.82

pH = 13.18

$[H^+] = 6.67 \times 10^{-14}\ M$

17.54 $2.0 \times 10^{-3}\ M$

17.56 The molarity of OH^- from the ionization water is 5.0×10^{-12} *M*.

17.58 6.49, 3.2×10^{-7}

17.60 0.43 %

17.62 $K_b = 1.5 \times 10^{-11}$

17.64 (a) $K_b = 7.1 \times 10^{-11}$ **(b)** Lactate ion is a weaker base

17.66 0.30 % ionized, $K_a = 1.8 \times 10^{-6}$

17.68 $K_a = 2.3 \times 10^{-2}$, $pK_a = 1.64$

17.70 $K_b = 5.5 \times 10^{-4}$, $pK_b = 3.23$

17.72 $[HC_3H_5O_2] = 0.145$

$[H^+] = 4.6 \times 10^{-3}$

$[C_3H_5O_2^-] = 4.6 \times 10^{-3}$

pH = 2.34

17.74 10.25

17.76 0.47 *M*

17.78 10.49

17.80 $[H^+] = 6.0 \times 10^{-4}$ *M*, pH = 3.22

17.82 pH = 11.30

$[HCN] = 2.0 \times 10^{-3}\ M$

17.84 pH = 5.72

17.86 $K_a = 1.4 \times 10^{-5}$

17.88 pH = 10.67

17.90 pH = 4.97

17.92 pH = 9.00

17.94 The concentration of NH_3 will decrease by 2.5×10^{-2} *M* and the NH_4^+ will increase by the same amount.

17.96 The pH of the solution changes –0.12 pH.

17.98 Initial pH = 9.36, final pH = 9.26, pH change = −0.1

17.100 2.2 g

17.102 Initial pH = 4.79, the final pH = 4.76, pH = 1.71

17.104 $[H_2C_6H_6O_6] \cong 0.15\ M$

$[H_3O^+] = [HC_6H_6O_6^-] = 3.5 \times 10^{-3}\ M$

$[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12}\ M$

pH = 2.50

17.106 $[H_3PO_4] = 2.0 - 0.12 = 1.9\ M$

$[H^+] = [H_2PO_3^-] = 0.12\ M$

$[HPO_4^{2-}] = 6.2 \times 10^{-8}$

$[PO_4^{3-}] = 2.2 \times 10^{-19}$

pH = −log(0.12) = 0.92

17.108 $0.20\ M = [H^+] = [H_2PO_3^-]$

$[HPO_3^{2-}] = 2.0 \times 10^{-7}\ M$

pH = 0.70

17.110 pH = 10.28

$[H_2SO_3] = 8.3 \times 10^{-13}$

$[HSO_3^-] = [OH^-] = 1.9 \times 10^{-4}\ M$

$[SO_3^{2-}] = 0.24\ M$ $[Na^+] = 0.24\ M$

$[H_3O^+] = 5.3 \times 10^{-11}$

17.112 pH = 9.70

17.114 pH = 12.99

$[H_3PO_4] = 2.1 \times 10^{-18}\ M$

$[H_2PO_4^-] = 1.6 \times 10^{-7}$

$[HPO_4^{2-}] = 9.8 \times 10^{-2}\ M$

17.116 pH = 8.07

17.118 pH = 12.93

17.120 (a) 2.87 **(b)** 4.44 **(c)** 4.74 **(d)** 8.72

| Chapter 18

Practice Exercises

18.1 $Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3+}(aq)$

$K_{sp} = [Ba^{2+}]^3[PO_4^{3+}]^2$

18.2 (a) $K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ **(b)** $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

18.3 3.2×10^{-10}

18.4 3.98×10^{-8}

18.5 2.78×10^{-18}

18.6 (a) 7.3×10^{-7} *M* **(b)** 1.3×10^{-4} *M*

18.7 4.5×10^{-5} *M*

18.8 2.1×10^{-16} *M* in 0.2 *M* CaI_2, 9.2×10^{-9} *M* in pure water

18.9 2.24×10^{-35} *M*

18.10 7.5×10^{-5}, a precipitate will form

18.11 7.8×10^{-13}, no precipitate will form

18.12 $PbSO_4$, precipitate will form

18.13 $PbCl_2$, no precipitate will form

18.14 $[SO_4^{2-}] > 2.2 \times 10^{-9}$ *M* and $[SO_4^{2-}] < 2.0 \times 10^{-4}$ *M*

18.15 $7.4 \times 10^{-6}\ M < [OH^-] < 5.0 \times 10^{-3}\ M$

18.16 CoS would precipitate

18.17 pH = 2.9
18.18 $[H^+] = 1.54 \times 10^{-1}$
18.19 Between pH = 5.34 and pH = 6.14
18.20 4.9×10^{-3} *M*, 1.3×10^{-5} *M*
18.21 4.1 mol

Review Problems

18.18 **(a)** $K_{sp} = [Ca^{2+}][F^-]^2$ **(d)** $K_{sp} = [Fe^{3+}][OH^-]^3$
(b) $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ **(e)** $K_{sp} = [Pb^{2+}][I^-]^2$
(c) $K_{sp} = [Pb^{2+}][SO_4^{2-}]$ **(f)** $K_{sp} = [Cu^{2+}][OH^-]^2$
18.20 $K_{sp} = (0.016)(0.032)^2 = 1.6 \times 10^{-5}$
18.22 1.05×10^{-5} *M*, $K_{sp} = 1.10 \times 10^{-10}$
18.24 $K_{sp} = 1.7 \times 10^{-6}$
18.26 $K_{sp} = 2.8 \times 10^{-18}$
18.28 $MgCO_3$
18.30 1.2×10^{-2} *M*
18.32 4.2×10^{-6} *M*
18.34 LiF
4.1×10^{-2} *M* = molar solubility of LiF
7.5×10^{-3} *M* = molar solubility of BaF_2
18.36 2.8×10^{-18}
18.38 7.0×10^{-3} moles/L
18.40 8.0×10^{-7}
18.42 **(a)** 4.1×10^{-4} *M* **(b)** 8.5×10^{-6} *M* **(c)** 8.5×10^{-7} *M*
(d) 5.7×10^{-7} *M*
18.44 5.6×10^{-9} *M*
18.46 $[Pb^{2+}] = 1.7 \times 10^{-3}$ *M*
18.48 **(a)** 3.0×10^{-11} moles/L **(b)** 1.2×10^{-6} moles/L
18.50 2.2 g $Fe(OH)_2$, $[Fe^{2+}] = 2.0 \times 10^{-12}$ *M*
18.52 4.9×10^{-8} *M*
18.54 No precipitate will form.
18.56 **(a)** No precipitate will form. **(b)** A precipitate will form.
18.58 A precipitate will not form.
18.60 2.3×10^{-8} *M*
18.62 $[H^+] = 0.045$ *M*, pH = 1.35
18.64 pH range = 4.8–8.1 $Mn(OH)_2$ will be soluble, but some $Cu(OH)_2$ will precipitate out of solution
18.66 pH range = 4.54–6.13
18.68
(a) $Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq)$

$$K_{\text{form}} = \frac{[CuCl_4^{2-}]}{[Cu^{2+}][Cl^-]^4}$$

(b) $Ag^+(aq) + 2I^-(aq) \rightleftharpoons AgI_2^-(aq)$ $K_{\text{form}} = \dfrac{[AgI_2^-]}{[Ag^+][I^-]^2}$

(c) $Cr^{3+}(aq) + 6NH_3(aq) \rightleftharpoons Cr(NH_3)_6^{3+}(aq)$

$$K_{\text{form}} = \frac{[Cr(NH_3)_6^{3+}]}{[Cr^{3+}][NH_3]^6}$$

18.70
(a) $Co^{3+}(aq) + 6NH_3(aq) \rightleftharpoons Co(NH_3)_6^{3+}(aq)$

$$K_{\text{form}} = \frac{[Co(NH_3)_6^{3+}]}{[Co^{3+}][NH_3]^6}$$

(b) $Hg^{2+}(aq) + 4I^-(aq) \rightleftharpoons HgI_4^{2-}(aq)$ $K_{\text{form}} = \dfrac{[HgI_4^{2-}]}{[Hg^{2+}][I^-]^4}$

(c) $Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$

$$K_{\text{form}} = \frac{[Fe(CN)_6^{4-}]}{[Fe^{2+}][CN^-]^6}$$

18.72 **(a)** $Co(NH_3)_6^{3+}(aq) \rightleftharpoons Co^{3+}(aq) + 6NH_3(aq)$
(b) $HgI_4^{2-}(aq) \rightleftharpoons Hg^{2+}(aq) + 4I^-(aq)$
(c) $Fe(CN)_6^{4-}(aq) \rightleftharpoons Fe^{2+}(aq) + 6CN^-(aq)$
18.74 4.3×10^{-4}
18.76 412 g NaCN
18.78 2.0×10^{-4} g AgI
18.80 4.9×10^{-3} *M*
18.82 3.7×10^{-11}

Chapter 19

Practice Exercises

19.1 +154 L atm
19.2 Energy is added to the system in the form of work.
19.3 −2.64 kJ ΔE is more exothermic
19.4 −214.6 kJ, 1%
19.5 Negative
19.6 **(a)** Negative **(b)** positive
19.7 **(a)** Negative **(b)** negative
19.8 **(a)** Negative **(b)** negative **(c)** positive
19.9 -99.1 J K^{-1}
19.10 **(a)** –229 J/K **(b)** –120.9 J/K
19.11 98.3 kJ mol^{-1}
19.12 −1482 kJ
19.13 −30.3 kJ
19.14 **(a)** –69.7 kJ/mol **(b)** –120.1 kJ/mol
19.15 3596 kJ work for $C_2H_5OH(l)$, 5803 kJ for $C_8H_{18}(l)$, C_8H_{18} is a better fuel on a gram basis.
19.16 788 kJ
19.17 +90.5 J K^{-1}
19.18 614 K (341 °C)
19.19 The reaction should be spontaneous
19.20 We do not expect to see products formed from reactants.
19.21 −4.3 kJ
19.22 +32.8 kJ, –34.7 kJ, the equilibrium shifts to products
19.23 $\Delta G = 0$ the system is at equilibrium
19.24 The reaction will proceed to the right
19.25 −33 kJ
19.26 0.26
19.27 −260.5 kJ for 1-propanol, −88 kJ for 2-bromobutane
19.28 −117 kJ for C_6H_{12}, +255.6 kJ for C_6H_6

Review Problems

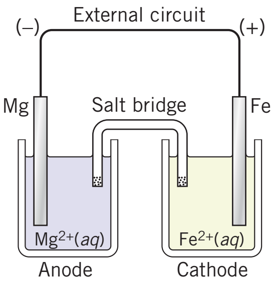
19.46 +1.000 kJ, endothermic
19.48 81 J
19.50 **(a)** $\Delta H° = +24.58$ kJ $\Delta E = 19.6$ kJ
(b) $\Delta H° = -178$ kJ $\Delta E = -175$ kJ
(c) $\Delta H° = 847.6$ kJ $\Delta E = \Delta H°$
(d) $\Delta H° = 65.029$ kJ $\Delta E = \Delta H°$
19.52 $\Delta E = -350$ kJ $\Delta E_{217\,°C} = -354$ kJ
19.54 **(a)** $\Delta H° = -178$ kJ, spontaneous **(b)** $\Delta H° = -311$ kJ, spontaneous **(c)** $\Delta H° = +1084.3$ kJ, not spontaneous
19.56 **(1)** The number of moles of products and reactants
(2) The state of the products versus reactants
(3) The complexity of the molecules
19.58 **(a)** Negative **(b)** negative **(c)** negative **(d)** positive
19.60 **(a)** –198.3 J/K, not spontaneous **(b)** –332.3 J/K, not spontaneous **(c)** +92.6 J/K, spontaneous **(d)** +14 J/K, spontaneous **(e)** +159 J/K, spontaneous

19.62 **(a)** –52.8 J mol^{-1} K^{-1} **(b)** –868.9 J mol^{-1} K^{-1} **(c)** –318 J mol^{-1} K^{-1}
19.64 −269.7 J/K
19.66 −209 kJ/mol
19.68 **(a)** −82.3 kJ **(b)** −8.8 kJ **(c)** +70.7 kJ
19.70 +0.16 kJ
19.72 −1299.8 kJ
19.74 333 K
19.76 101 J mol^{-1} K^{-1}
19.78 Spontaneous
19.80 **(a)** $K_p = 3.63 \times 10^{43}$ **(b)** $K_p = 5.37 \times 10^{-13}$
19.82 The system is not at equilibrium and must shift to the right to reach equilibrium.
19.84 $K_p = 8.000 \times 10^8$
This is a favorable reaction, since the equilibrium lies far to the side favoring products and is worth studying as a method for methane production.
19.86 If $\Delta G° = 0$, $K_c = 1$. If we start with pure products, the value of Q will be infinite (there are zero reactants) and, since $Q > K_c$, the equilibrium will shift toward the reactants, i.e., the pure products will decompose to their reactants.
19.88 1.16×10^3 kJ/mol
19.90 354 kJ/mol
19.92 577.7 kJ/mol
19.94 308.0 kJ/mol
19.96 85 kJ/mol
19.98 The heat of formation of CF_4 should be more exothermic than that of CCl_4 because more energy is released on formation of a C—F bond than on formation of a C—Cl bond. Also, less energy is needed to form gaseous F atoms than to form gaseous Cl atoms.

Chapter 20

Practice Exercises

20.1 Anode: $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Cathode: $Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
Cell notation: $Mg(s) \mid Mg^{2+}(aq) \parallel Fe^{2+}(aq) \mid Fe(s)$



20.2 Anode: $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Cathode: $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
Overall: $3Ni^{2+}(aq) + 2Al(s) \longrightarrow 2Al^{3+}(aq) + 3Ni(s)$
20.3 Zinc
20.4 −0.44 V
20.5 **(a)** $2I^-(aq) + 2Fe^{3+}(aq) \longrightarrow I_2(aq) + 2Fe^{2+}(aq)$
(b) $3Mg(s) + 2Cr^{3+}(aq) \longrightarrow 3Mg^{2+}(aq) + 2Cr(s)$
(c) $SO_4^{2-}(aq) + 4H^+(aq) + Co(s) \longrightarrow H_2SO_3(aq) + H_2O + Co^{2+}(aq)$
20.6 $Br_2(aq) + H_2SO_3(aq) + H_2O \longrightarrow 2Br^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$
20.7 Non-spontaneous
$Ni(s) + 2Fe^{3+}(aq) \longrightarrow Ni^{2+}(aq) + 2Fe^{2+}(aq)$
20.8 $NiO_2(s) + Fe(s) + 2H_2O \longrightarrow Ni(OH)_2(s) + Fe(OH)_2(s)$ $E°_{cell} = 1.37$ V
20.9 $5Cr(s) + 3MnO_4^-(aq) + 24H^+(aq) \longrightarrow 3Mn^{2+}(aq) + 12H_2O(l) + 5Cr^{3+}(aq)$ $E°_{cell} = 2.25$ V
20.10 $3Cu^{2+}(aq) + 2Cr(s) \longrightarrow 3Cu(s) + 2Cr^{3+}(aq)$ $E°_{cell} = 1.08$ V
20.11 **(a)** Spontaneous **(b)** spontaneous
20.12 **(a)** Non-spontaneous **(b)** spontaneous
20.13 3 electrons
20.14 For 20.11 **(a)** –102 kJ **(b)** –343 kJ
For 20.12 **(a)** 108 kJ **(b)** –11.6 kJ
20.15 $K_c = 2.7 \times 10^{-16}$, $K = 3.7 \times 10^{15}$
20.16 $K = \dfrac{1}{[Ag^+][Br^-]}$
2.23×10^{12}
20.17 $Cu^{2+}(aq) + Mg(s) \longrightarrow Cu(s) + Mg^{2+}(aq)$ 2.82 V
20.18 pH = 2.37
20.19 1.04 V
20.20 $[Mg^{2+}] = 2.95 \times 10^{-5}$ *M*
20.21 Sample 1 (0.57 V): $[Cu^{2+}] = 9.6 \times 10^{-6}$ *M*,
sample 2 (0.82 V): $[Cu^{2+}] = 3.4 \times 10^{-14}$ *M*
20.22 $[Cr^{3+}] = 6.6 \times 10^{-4}$ *M*
20.23 I_2 will be produced at the anode
20.24 Sn(s) will be produced at the cathode
20.25 7.46×10^{-3} mol OH^-
20.26 7.33 min
20.27 3.67 A
20.28 0.0187 *M*

Review Problems

20.50 **(a)** $Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^-$
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$
$3Cd(s) + 2Au^{3+}(aq) \longrightarrow 3Cd^{2+}(aq) + 2Au(s)$
(b) $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$
$Fe(s) + Br_2(aq) \longrightarrow Fe^{2+}(aq) + 2Br^-(aq)$
(c) $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
$2Cr(s) + 3Cu^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cu(s)$
20.52 **(a)** $Pt(s) \mid Fe^{2+}(aq), Fe^{3+}(aq) \parallel NO_3^-(aq), H^+(aq) \mid NO(g) \mid Pt(s)$
(b) $Pt(s) \mid Br_2(aq), Br^-(aq) \parallel Cl^-(aq), Cl_2(g) \mid Pt(s)$
(c) $Ag(s) \mid Ag^+(aq) \parallel Au^{3+}(aq) \mid Au(s)$
20.54 **(a)** Sn(*s*) **(b)** $Br^-(aq)$ **(c)** Zn(*s*) **(d)** $I^-(aq)$
20.56 **(a)** $E°_{cell} = 0.19$ V **(b)** $E°_{cell} = -0.29$ V **(c)** $E°_{cell} = 0.62$ V
20.58 **(a)** Spontaneous **(b)** spontaneous **(c)** spontaneous
20.60 $BrO_3^-(aq) + 6I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(s) + Br^-(aq) + 3H_2O$, $E_c = 0.90$ V
20.62 $4HOCl(aq) + 2H^+(aq) + S_2O_3^{2-}(aq) \longrightarrow 2Cl_2(g) + H_2O + 2H_2SO_3(aq)$
20.64 Non-spontaneous
20.66 1.0×10^2 kJ
20.68 **(a)** $E°_{cell} = 0.54$ V **(b)** -5.2×10^2 kJ **(c)** 2.1×10^{91}
20.70 0.31
20.72 2.38 V
20.74 $[Cd^{2+}] = 2.86 \times 10^{-15}$ *M*
20.76 $K_{sp} = 8.66 \times 10^{-14}$

20.78 $E^\circ_{\text{cell}} = 0.090$ V $E^{348\,K}_{\text{cell}} = 0.105$ V
20.80 **(a)** 0.40 mol e^- **(b)** 0.70 mol e^- **(c)** 4.50 mol e^- **(d)** 5.0×10^{-2} mol e^-
20.82 2.68 g $Fe(OH)_2$
20.84 51.5 hr
20.86 66.2 amp
20.88 0.0996 *M*
20.90 H_2 and O_2, $2H_2O \longrightarrow 2H_2(g) + O_2(g)$
20.92 Cu and Br_2, $Cu^{2+} + 2Br^- \longrightarrow Br_2 + Cu(s)$
20.94 Al^{3+}, Mg^{2+}, Na^+, Ca^{2+}, K^+, and Li^+

Chapter 21

Practice Exercises

21.1 45.9 g
21.2 46.5 g
21.3 0.166974 u
21.4 9.965×10^{-12} J/nucleon
21.5 ${}^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He} + {}^{0}_{0}\gamma$ An alpha particle is emitted.
21.6 ${}^{90}_{38}\text{Sr} \longrightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}e$
21.7 ${}^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}e + \nu$
21.8 ${}^{13}_{4}\text{Be} \longrightarrow {}^{12}_{4}\text{Be} + {}^{1}_{0}n$
21.9 ${}^{72}_{34}\text{Se} + {}^{0}_{-1}e \longrightarrow {}^{72}_{33}\text{As} + \text{X ray} + \nu$
21.10 ${}^{242}_{96}\text{Cm} \longrightarrow {}^{238}_{94}\text{Pu} + {}^{4}_{2}\text{He}$
21.11 ${}^{56}_{26}\text{Fe} \longrightarrow {}^{59}_{27}\text{Co} + {}^{0}_{-1}e$
21.12 50.4% Pu
21.13 7.36×10^4 atoms ${}^{222}\text{Rn}$
21.14 20 m
21.15 100 units

Review Problems

21.48 **(a)** 1.01 kg **(b)** 3.91 kg **(c)** 12.3 kg
21.50 1.11×10^{-11} g
21.52 3.18 ng, 1.77×10^{-8}%
21.54 1.8×10^{-13} J per nucleon
21.56 0.5526646 u, 8.2485×10^{-11} J
21.58 **(a)** ${}^{211}_{83}\text{Bi}$ **(b)** ${}^{177}_{72}\text{Hf}$ **(c)** ${}^{216}_{84}\text{Po}$ **(d)** ${}^{19}_{9}\text{F}$
21.60 **(a)** ${}^{242}_{94}\text{Pu} \longrightarrow {}^{4}_{2}\text{He} + {}^{238}_{92}\text{U}$
  (b) ${}^{28}_{12}\text{Mg} \longrightarrow {}^{0}_{-1}e + {}^{28}_{13}\text{Al}$
  (c) ${}^{26}_{14}\text{Si} \longrightarrow {}^{0}_{1}e + {}^{26}_{13}\text{Al}$
  (d) ${}^{37}_{18}\text{Ar} \longrightarrow {}^{0}_{-1}e + {}^{37}_{17}\text{Cl}$
21.62 **(a)** ${}^{261}_{102}\text{No}$ **(b)** ${}^{211}_{82}\text{Pb}$ **(c)** ${}^{141}_{61}\text{Pm}$ **(d)** ${}^{179}_{74}\text{W}$
21.64 ${}^{87}_{36}\text{Kr} \longrightarrow {}^{86}_{36}\text{Kr} + {}^{1}_{0}n$
21.66 The more likely process is positron emission, because this produces a product having a higher neutron-to-proton ratio:
${}^{38}_{19}\text{K} \longrightarrow {}^{0}_{1}e + {}^{38}_{18}\text{Ar}$
21.68 ${}^{209}_{84}\text{Po} \longrightarrow {}^{205}_{82}\text{Pb} + {}^{4}_{2}\text{He}$
21.70 0.0469 mg
21.72 ${}^{53}_{24}\text{Cr}^*$ forms. The reaction is:
${}^{51}_{23}\text{V} + {}^{2}_{1}\text{H} \longrightarrow {}^{53}_{24}\text{Cr}^* \longrightarrow {}^{1}_{1}p + {}^{52}_{23}\text{V}$
21.74 ${}^{80}_{35}\text{Br}$
21.76 ${}^{55}_{26}\text{Fe}$; ${}^{55}_{25}\text{Mn} + {}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{55}_{26}\text{Fe}$
21.78 ${}^{70}_{30}\text{Zn} + {}^{208}_{82}\text{Pb} \longrightarrow {}^{278}_{112}\text{Uub} \longrightarrow {}^{1}_{0}n + {}^{277}_{112}\text{Uub}$
21.80 6.3 m
21.82 6.6 m
21.84 This is one curie. It is also 3.7×10^{10} Bq
21.86 2.4×10^7 Bq, 650 μCi
21.88 6.9×10^5 s
21.90 3.2%
21.92 2.84×10^{-3} Ci/g
21.94 1.3×10^9 years old
21.96 2.7×10^4 yr
21.98 ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{94}_{38}\text{Sr} + {}^{140}_{54}\text{Xe} + 2\,{}^{1}_{0}n$

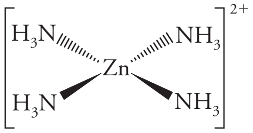
Chapter 22

Practice Exercises

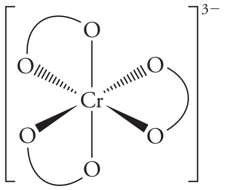
22.1 $[Ag(S_2O_3)_2]^{3-}$ $(NH_4)_3Ag(S_2O_3)_2$
22.2 $AlCl_3 \cdot 6H_2O$ $[Al(H_2O)_6]^{3+}$
22.3 $[CrCl_2(H_2O)_4]^+$ The counter ion would be a halide
22.4 **(a)** $[SnCl_6]^{2-}$
  (b) $(NH_4)_2[Fe(CN)_4(H_2O)_2]$
  (c) $OsBr_2(H_2NCH_2CH_2NH_2)_2$ or $OsBr_2(en)_2$
22.5 **(a)** potassium hexacyanoferrate(III)
  (b) dichlorobis(ethylenediamine)chromium(III) sulfate
  (c) hexaaquacobalt(II) hexafluorochromate(II)
22.6 Six
22.7 **(a)** six **(b)** six **(c)** six
22.8 **(a)** four, square planar **(b)** two, linear

Review Problems

22.40 The net charge is –3, and the formula is $[Fe(CN)_6]^{3-}$, hexacyanoferrate(III) ion
22.42 $[CoCl_2(en)_2]^+$
22.44 **(a)** $C_2O_4{}^{2-}$ oxalato **(b)** S^{2-} sulfido or thio **(c)** Cl^- chloro **(d)** $(CH_3)_2NH$ dimethylamine
22.46 **(a)** hexaamminenickel(II) chloride
  (b) triamminetrichlorochromate(II) ion
  (c) hexanitrocobaltate(III) ion
  (d) diamminetetracyanomanganate(II) ion
  (e) potassium trioxalatoferrate(III) or potassium trisoxalatoferrate(III)
22.48 **(a)** $[Fe(CN)_2(H_2O)_4]^+$
  (b) $[Ni(C_2O_4)(NH_3)_4]$
  (c) $[Al(OH)(H_2O)_5]Cl_2$
  (d) $K_3[Mn(SCN)_6]$
  (e) $[CuCl_4]^{2-}$
22.50 Coordination number is six, oxidation number is +2.
22.52 **(a)**

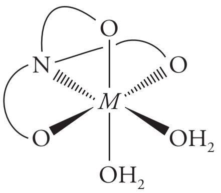


(b)



The curved lines represent the backbone of the oxalate ion.

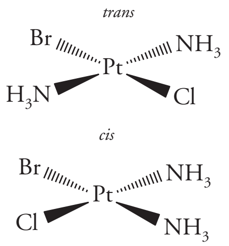
22.54



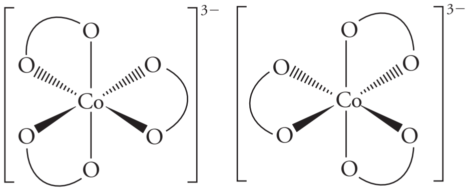
The curved lines represent —CH_2—C(=O)— groups.

22.56 Since both are the *cis* isomer, they are identical.

22.58



22.60



22.62 **(a)** $[Cr(H_2O)_6]^{3+}$ **(b)** $[Cr(en)_3]^{3+}$
22.64 $[Cr(CN)_6]^{3-}$
22.66 **(a)** $[RuCl(NH_3)_5]^{3+}$
(b) $[Ru(NH_3)_6]^{3+}$

22.68 CoA_6^{2+}, A produces a larger crystal filed splitting than B, so you are removing a higher energy electron in CoA_6^{2+} than in CoB_6^{2+}.

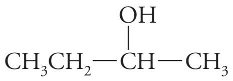
22.70 High-spin d^7; it cannot be diamagnetic.

Chapter 23

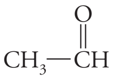
Practice Exercises

23.1 2,2-dimethylpropane
23.2 **(a)** 3-methylhexane
(b) 4-ethyl-2,3-dimethylheptane
(c) 5-ethyl-2,4,6-trimethyloctane

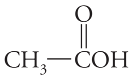
23.3


$CH_3CH_2-\overset{OH}{\overset{|}{C}}H-CH_3$

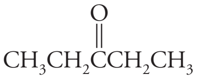
23.4 **(a)**


$CH_3-\overset{O}{\overset{\|}{C}}H$

or

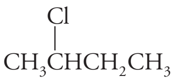

$CH_3-\overset{O}{\overset{\|}{C}}OH$

(b)


$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

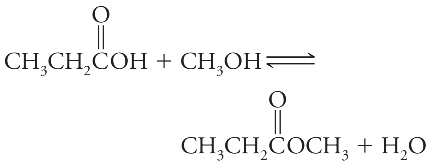
(c) Tertiary alcohols do not undergo oxidation in the same manner as primary and secondary alcohols.

23.5 **(a)**


$CH_3\overset{Cl}{\overset{|}{C}}HCH_2CH_3$

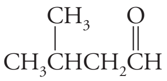
(b) $CH_3CH{=}CH_2$

23.6

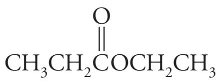

$CH_3CH_2\overset{O}{\overset{\|}{C}}OH + CH_3OH \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3 + H_2O$

methylpropanoate

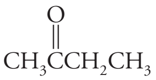
23.7 **(a)**


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}H$

(b)

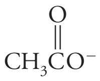

$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

(c)

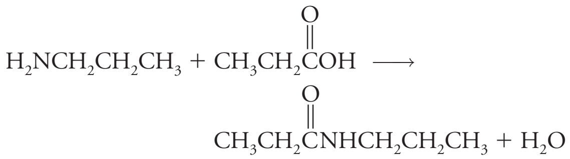

$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$

23.8

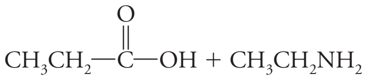
CH_3CH_2OH and


$CH_3\overset{O}{\overset{\|}{C}}O^-$

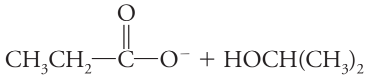
23.9


$H_2NCH_2CH_2CH_3 + CH_3CH_2\overset{O}{\overset{\|}{C}}OH \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2CH_3 + H_2O$

23.10 **(a)**

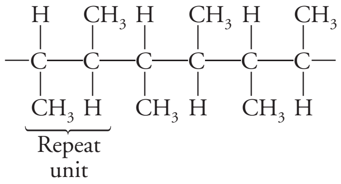

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_3CH_2NH_2$

(b)

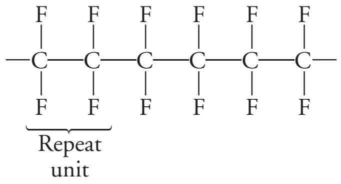

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O^- + HOCH(CH_3)_2$

(c) $CH_3CH_2CH{=}CH_2$

23.11

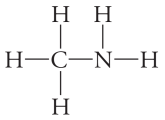


23.12

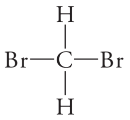


Review Problems

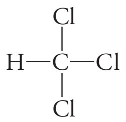
23.91 **(a)**



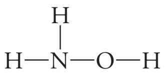
(b)



(c)

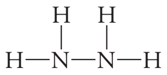


(d)



(e) $H-C\equiv C-H$

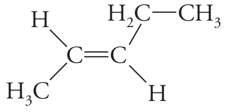
(f)



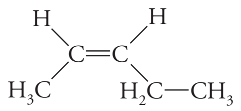
23.93 **(a)** alkene **(d)** carboxylic acid
(b) alcohol **(e)** amine
(c) ester **(f)** alcohol
23.95 b, e, and f
23.97 **(a)** amine **(b)** amine **(c)** amide **(d)** amine, ketone
23.99 **(a)** Identical **(b)** identical **(c)** unrelated
(d) isomers **(e)** identical **(f)** identical
(g) isomers
23.101 **(a)** pentane **(b)** 2-methylpentane **(c)** 2,4-dimethylhexane

23.103 **(a)** No isomers

(b)

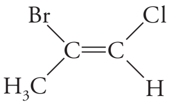


trans

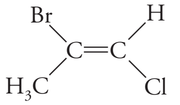


cis

(c)



cis

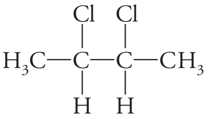


trans

23.105 **(a)** CH_3CH_3 **(b)** $ClCH_2CH_2Cl$ **(c)** $BrCH_2CH_2Br$
(d) CH_3CH_2Cl **(e)** CH_3CH_2Br **(f)** CH_3CH_2OH

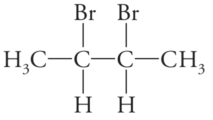
23.107 **(a)** $CH_3CH_2CH_2CH_3$

(b)



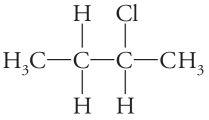
$\mathrm{H_3C-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3}$

(c)



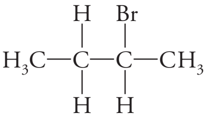
$\mathrm{H_3C-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}-CH_3}$

(d)



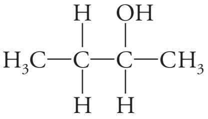
$\mathrm{H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3}$

(e)



$\mathrm{H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-CH_3}$

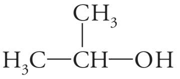
(f)



$\mathrm{H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-CH_3}$

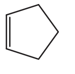
23.109 This sort of reaction would disrupt the π delocalization of the benzene ring. The subsequent loss of resonance energy would not be favorable.

23.111

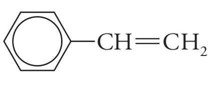
CH_3OH	IUPAC name = methanol;	common name = methyl alcohol
CH_3CH_2OH	IUPAC name = ethanol;	common name = ethyl alcohol
$CH_3CH_2CH_2OH$	IUPAC name = 1-propanol;	common name = propyl alcohol
$(CH_3)_2COH$ or as shown below  $\mathrm{H_3C-\overset{CH_3}{CH}-OH}$	IUPAC name = 2-propanol;	common name = isopropyl alcohol

23.113 $CH_3CH_2CH_2-O-CH_3$ methyl propyl ether
$CH_3CH_2-O-CH_2CH_3$ diethyl ether
$(CH_3)_2CH-O-CH_3$ methyl 2-propyl ether

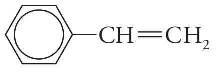
23.115 **(a)**



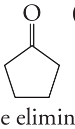
(b)



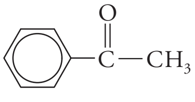
(c)



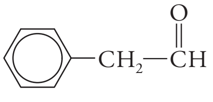
23.117 **(a)**



(b)



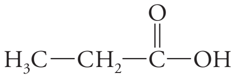
(c)



23.119 The elimination of water can result in a C═C double bond in two locations:

$CH_2{=}CHCH_2CH_3$ $CH_3CH{=}CHCH_3$
1-butene 2-butene

23.121 The aldehyde is more easily oxidized. The product is:

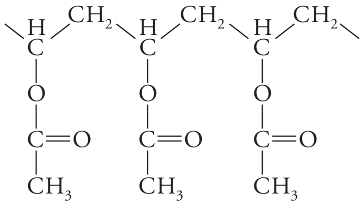


$\mathrm{H_3C-CH_2-\overset{O}{\overset{\|}{C}}-OH}$

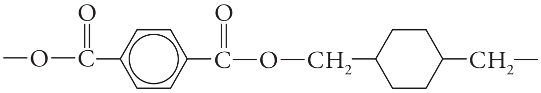
23.123 **(a)** $CH_3CH_2CO_2H$
(b) $CH_3CH_2CO_2H + CH_3OH$
(c) $Na^+ + CH_3CH_2CH_2CO_2^- + H_2O$

23.125 $CH_3CO_2H + CH_3CH_2NHCH_2CH_3$

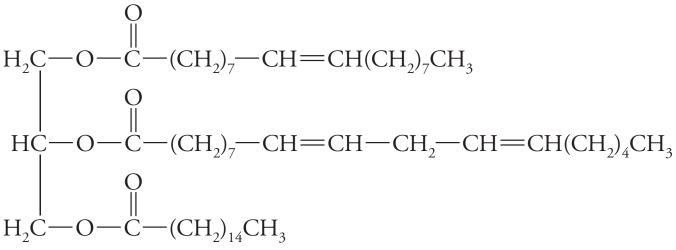
23.127



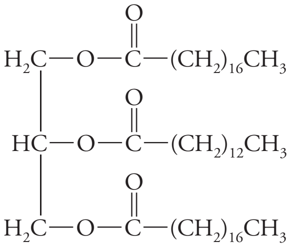
23.129



23.131

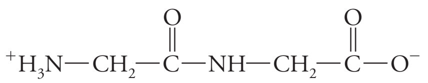


23.133



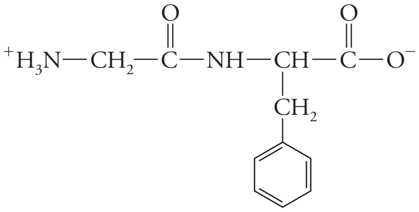
23.135 Hydrophobic sites are composed of fatty acid units. Hydrophilic sites are composed of charged units.

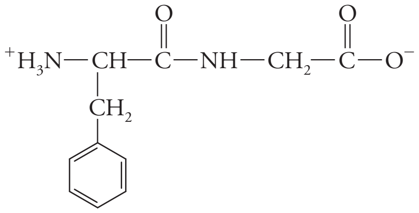
23.137



$\mathrm{{}^+H_3N-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{O}{\overset{\|}{C}}-O^-}$

23.139





Appendix C

Tables of Selected Data

Table C.1 Electron Configurations of the Elements

Atomic Number			Atomic Number			Atomic Number		
1	H	$1s^1$	41	Nb	[Kr] $5s^1\,4d^4$	81	Tl	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^1$
2	He	$1s^2$	42	Mo	[Kr] $5s^1\,4d^5$	82	Pb	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^2$
3	Li	[He] $2s^1$	43	Tc	[Kr] $5s^2\,4d^5$	83	Bi	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^3$
4	Be	[He] $2s^2$	44	Ru	[Kr] $5s^1\,4d^7$	84	Po	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^4$
5	B	[He] $2s^2\,2p^1$	45	Rh	[Kr] $5s^1\,4d^8$	85	At	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^5$
6	C	[He] $2s^2\,2p^2$	46	Pd	[Kr] $4d^{10}$	86	Rn	[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^6$
7	N	[He] $2s^2\,2p^3$	47	Ag	[Kr] $5s^1\,4d^{10}$	87	Fr	[Rn] $7s^1$
8	O	[He] $2s^2\,2p^4$	48	Cd	[Kr] $5s^2\,4d^{10}$	88	Ra	[Rn] $7s^2$
9	F	[He] $2s^2\,2p^5$	49	In	[Kr] $5s^2\,4d^{10}\,5p^1$	89	Ac	[Rn] $7s^2\,6d^1$
10	Ne	[He] $2s^2\,2p^6$	50	Sn	[Kr] $5s^2\,4d^{10}\,5p^2$	90	Th	[Rn] $7s^2\,6d^2$
11	Na	[Ne] $3s^1$	51	Sb	[Kr] $5s^2\,4d^{10}\,5p^3$	91	Pa	[Rn] $7s^2\,5f^2\,6d^1$
12	Mg	[Ne] $3s^2$	52	Te	[Kr] $5s^2\,4d^{10}\,5p^4$	92	U	[Rn] $7s^2\,5f^3\,6d^1$
13	Al	[Ne] $3s^2\,3p^1$	53	I	[Kr] $5s^2\,4d^{10}\,5p^5$	93	Np	[Rn] $7s^2\,5f^4\,6d^1$
14	Si	[Ne] $3s^2\,3p^2$	54	Xe	[Kr] $5s^2\,4d^{10}\,5p^6$	94	Pu	[Rn] $7s^2\,5f^6$
15	P	[Ne] $3s^2\,3p^3$	55	Cs	[Xe] $6s^1$	95	Am	[Rn] $7s^2\,5f^7$
16	S	[Ne] $3s^2\,3p^4$	56	Ba	[Xe] $6s^2$	96	Cm	[Rn] $7s^2\,5f^7\,6d^1$
17	Cl	[Ne] $3s^2\,3p^5$	57	La	[Xe] $6s^2\,5d^1$	97	Bk	[Rn] $7s^2\,5f^9$
18	Ar	[Ne] $3s^2\,3p^6$	58	Ce	[Xe] $6s^2\,4f^1\,5d^1$	98	Cf	[Rn] $7s^2\,5f^{10}$
19	K	[Ar] $4s^1$	59	Pr	[Xe] $6s^2\,4f^3$	99	Es	[Rn] $7s^2\,5f^{11}$
20	Ca	[Ar] $4s^2$	60	Nd	[Xe] $6s^2\,4f^4$	100	Fm	[Rn] $7s^2\,5f^{12}$
21	Sc	[Ar] $4s^2\,3d^1$	61	Pm	[Xe] $6s^2\,4f^5$	101	Md	[Rn] $7s^2\,5f^{13}$
22	Ti	[Ar] $4s^2\,3d^2$	62	Sm	[Xe] $6s^2\,4f^6$	102	No	[Rn] $7s^2\,5f^{14}$
23	V	[Ar] $4s^2\,3d^3$	63	Eu	[Xe] $6s^2\,4f^7$	103	Lr	[Rn] $7s^2\,5f^{14}\,6d^1$
24	Cr	[Ar] $4s^1\,3d^5$	64	Gd	[Xe] $6s^2\,4f^7\,5d^1$	104	Rf	[Rn] $7s^2\,5f^{14}\,6d^2$
25	Mn	[Ar] $4s^2\,3d^5$	65	Tb	[Xe] $6s^2\,4f^9$	105	Db	[Rn] $7s^2\,5f^{14}\,6d^3$
26	Fe	[Ar] $4s^2\,3d^6$	66	Dy	[Xe] $6s^2\,4f^{10}$	106	Sg	[Rn] $7s^2\,5f^{14}\,6d^4$
27	Co	[Ar] $4s^2\,3d^7$	67	Ho	[Xe] $6s^2\,4f^{11}$	107	Bh	[Rn] $7s^2\,5f^{14}\,6d^5$
28	Ni	[Ar] $4s^2\,3d^8$	68	Er	[Xe] $6s^2\,4f^{12}$	108	Hs	[Rn] $7s^2\,5f^{14}\,6d^6$
29	Cu	[Ar] $4s^1\,3d^{10}$	69	Tm	[Xe] $6s^2\,4f^{13}$	109	Mt	[Rn] $7s^2\,5f^{14}\,6d^7$
30	Zn	[Ar] $4s^2\,3d^{10}$	70	Yb	[Xe] $6s^2\,4f^{14}$	110	Ds	[Rn] $7s^2\,5f^{14}\,6d^8$
31	Ga	[Ar] $4s^2\,3d^{10}\,4p^1$	71	Lu	[Xe] $6s^2\,4f^{14}\,5d^1$	111	Rg	[Rn] $7s^2\,5f^{14}\,6d^9$
32	Ge	[Ar] $4s^2\,3d^{10}\,4p^2$	72	Hf	[Xe] $6s^2\,4f^{14}\,5d^2$	112	Cn	[Rn] $7s^2\,5f^{14}\,6d^{10}$
33	As	[Ar] $4s^2\,3d^{10}\,4p^3$	73	Ta	[Xe] $6s^2\,4f^{14}\,5d^3$	113	Uut	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^1$
34	Se	[Ar] $4s^2\,3d^{10}\,4p^4$	74	W	[Xe] $6s^2\,4f^{14}\,5d^4$	114	Uuq	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^2$
35	Br	[Ar] $4s^2\,3d^{10}\,4p^5$	75	Re	[Xe] $6s^2\,4f^{14}\,5d^5$	115	Uup	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^3$
36	Kr	[Ar] $4s^2\,3d^{10}\,4p^6$	76	Os	[Xe] $6s^2\,4f^{14}\,5d^6$	116	Uuh	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^4$
37	Rb	[Kr] $5s^1$	77	Ir	[Xe] $6s^2\,4f^{14}\,5d^7$	117	Uus	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^5$
38	Sr	[Kr] $5s^2$	78	Pt	[Xe] $6s^1\,4f^{14}\,5d^9$	118	Uuo	[Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^6$
39	Y	[Kr] $5s^2\,4d^1$	79	Au	[Xe] $6s^1\,4f^{14}\,5d^{10}$			
40	Zr	[Kr] $5s^2\,4d^2$	80	Hg	[Xe] $6s^2\,4f^{14}\,5d^{10}$			

Table C.2 Thermodynamic Data for Selected Elements, Compounds, and Ions (25 °C)

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	ΔG_f° (kJ mol^{-1})
Aluminum			
$\mathrm{Al}(s)$	0	28.3	0
$\mathrm{Al}^{3+}(aq)$	−524.7		−481.2
$\mathrm{AlCl_3}(s)$	−704	110.7	−629
$\mathrm{Al_2O_3}(s)$	−1669.8	51.0	−1576.4
$\mathrm{Al_2(SO_4)_3}(s)$	−3441	239	−3100
Arsenic			
$\mathrm{As}(s)$	0	35.1	0
$\mathrm{AsH_3}(g)$	+66.4	223	+68.9
$\mathrm{As_4O_6}(s)$	−1314	214	−1153
$\mathrm{As_2O_5}(s)$	−925	105	−782
$\mathrm{H_3AsO_3}(aq)$	−742.2		
$\mathrm{H_3AsO_4}(aq)$	−902.5		
Barium			
$\mathrm{Ba}(s)$	0	66.9	0
$\mathrm{Ba}^{2+}(aq)$	−537.6	9.6	−560.8
$\mathrm{BaCO_3}(s)$	−1219	112	−1139
$\mathrm{BaCrO_4}(s)$	−1428.0		
$\mathrm{BaCl_2}(s)$	−860.2	125	−810.8
$\mathrm{BaO}(s)$	−553.5	70.4	−525.1
$\mathrm{Ba(OH)_2}(s)$	−998.22	−8	−875.3
$\mathrm{Ba(NO_3)_2}(s)$	−992	214	−795
$\mathrm{BaSO_4}(s)$	−1465	132	−1353
Beryllium			
$\mathrm{Be}(s)$	0	9.50	0
$\mathrm{BeCl_2}(s)$	−468.6	89.9	−426.3
$\mathrm{BeO}(s)$	−611	14	−582
Bismuth			
$\mathrm{Bi}(s)$	0	56.9	0
$\mathrm{BiCl_3}(s)$	−379	177	−315
$\mathrm{Bi_2O_3}(s)$	−576	151	−497
Boron			
$\mathrm{B}(s)$	0	5.87	0
$\mathrm{BCl_3}(g)$	−404	290	−389
$\mathrm{B_2H_6}(g)$	+36	232	+87
$\mathrm{B_2O_3}(s)$	−1273	53.8	−1194
$\mathrm{B(OH)_3}(s)$	−1094	88.8	−969
Bromine			
$\mathrm{Br_2}(l)$	0	152.2	0
$\mathrm{Br_2}(g)$	+30.9	245.4	+3.11
$\mathrm{HBr}(g)$	−36	198.5	+53.1
$\mathrm{Br}^-(aq)$	−121.55	82.4	−103.96
Cadmium			
$\mathrm{Cd}(s)$	0	51.8	0
$\mathrm{Cd}^{2+}(aq)$	−75.90	−73.2	−77.61
$\mathrm{CdCl_2}(s)$	−392	115	−344
$\mathrm{CdO}(s)$	−258.2	54.8	−228.4
$\mathrm{CdS}(s)$	−162	64.9	−156
$\mathrm{CdSO_4}(s)$	−933.5	123	−822.6
Calcium			
$\mathrm{Ca}(s)$	0	41.4	0
$\mathrm{Ca}^{2+}(aq)$	−542.83	−53.1	−553.58
$\mathrm{CaCO_3}(s)$	−1207	92.9	−1128.8
$\mathrm{CaF_2}(s)$	−741	80.3	−1166
$\mathrm{CaCl_2}(s)$	−795.0	114	−750.2
$\mathrm{CaBr_2}(s)$	−682.8	130	−663.6
$\mathrm{CaI_2}(s)$	−535.9	143	
$\mathrm{CaO}(s)$	−635.5	40	−604.2
$\mathrm{Ca(OH)_2}(s)$	−986.59	76.1	−896.76
$\mathrm{Ca_3(PO_4)_2}(s)$	−4119	241	−3852
$\mathrm{CaSO_3}(s)$	−1156		
$\mathrm{CaSO_4}(s)$	−1433	107	−1320.3
$\mathrm{CaSO_4 \cdot \frac{1}{2}H_2O}(s)$	−1575.2	131	−1435.2
$\mathrm{CaSO_4 \cdot 2H_2O}(s)$	−2021.1	194.0	−1795.7
Carbon			
$\mathrm{C}(s,$ graphite$)$	0	5.69	0
$\mathrm{C}(s,$ diamond$)$	+1.88	2.4	+2.9
$\mathrm{CCl_4}(l)$	−134	214.4	−65.3
$\mathrm{CO}(g)$	−110.5	197.9	−137.3
$\mathrm{CO_2}(g)$	−393.5	213.6	−394.4
$\mathrm{CO_2}(aq)$	−413.8	117.6	−385.98
$\mathrm{H_2CO_3}(aq)$	−699.65	187.4	−623.08
$\mathrm{HCO_3}^-(aq)$	−691.99	91.2	−586.77
$\mathrm{CO_3}^{2-}(aq)$	−677.14	−56.9	−527.81
$\mathrm{CS_2}(l)$	+89.5	151.3	+65.3
$\mathrm{CS_2}(g)$	+117	237.7	+67.2
$\mathrm{HCN}(g)$	+135.1	201.7	+124.7
$\mathrm{CN}^-(aq)$	+150.6	94.1	+172.4
$\mathrm{CH_4}(g)$	−74.848	186.2	−50.79
$\mathrm{C_2H_2}(g)$	+226.75	200.8	+209
$\mathrm{C_2H_4}(g)$	+52.284	219.8	+68.12
$\mathrm{C_2H_6}(g)$	−84.667	229.5	−32.9
$\mathrm{C_3H_8}(g)$	−104	269.9	−23
$\mathrm{C_4H_{10}}(g)$	−126	310.2	−17.0
$\mathrm{C_6H_6}(l)$	+49.0	173.3	+124.3
$\mathrm{CH_3OH}(l)$	−238.6	126.8	−166.2
$\mathrm{C_2H_5OH}(l)$	−277.63	161	−174.8
$\mathrm{HCHO_2}(g)$	−363	251	+335
$\mathrm{HC_2H_3O_2}(l)$	−487.0	160	−392.5
$\mathrm{HCHO}(g)$	−108.6	218.8	−102.5
$\mathrm{CH_3CHO}(g)$	−167	250	−129

(Continued)

Table C.2 **Thermodynamic Data for Selected Elements, Compounds, and Ions (25 °C)** *(Continued)*

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	ΔG_f° (kJ mol^{-1})
$(CH_3)_2CO(l)$	−248.1	200.4	−155.4
$C_6H_5CO_2H(s)$	−385.1	167.6	−245.3
$CO(NH_2)_2(s)$	−333.19	104.6	−197.2
$CO(NH_2)_2(aq)$	−391.2	173.8	−203.8
$CH_2(NH_2)CO_2H(s)$	−532.9	103.5	−373.4
Chlorine			
$Cl_2(g)$	0	223.0	0
$Cl^-(aq)$	−167.2	56.5	−131.2
$HCl(g)$	−92.30	186.7	−95.27
$HCl(aq)$	−167.2	56.5	−131.2
$HClO(aq)$	−131.3	106.8	−80.21
Chromium			
$Cr(s)$	0	23.8	0
$Cr^{3+}(aq)$	−232		
$CrCl_2(s)$	−326	115	−282
$CrCl_3(s)$	−563.2	126	−493.7
$Cr_2O_3(s)$	−1141	81.2	−1059
$CrO_3(s)$	−585.8	72.0	−506.2
$(NH_4)_2Cr_2O_7(s)$	−1807		
$K_2Cr_2O_7(s)$	−2033.01		
Cobalt			
$Co(s)$	0	30.0	0
$Co^{2+}(aq)$	−59.4	−110	−53.6
$CoCl_2(s)$	−325.5	106	−282.4
$Co(NO_3)_2(s)$	−422.2	192	−230.5
$CoO(s)$	−237.9	53.0	−214.2
$CoS(s)$	−80.8	67.4	−82.8
Copper			
$Cu(s)$	0	33.15	0
$Cu^{2+}(aq)$	+64.77	−99.6	+65.49
$CuCl(s)$	−137.2	86.2	−119.87
$CuCl_2(s)$	−172	119	−131
$Cu_2O(s)$	−168.6	93.1	−146.0
$CuO(s)$	−155	42.6	−127
$Cu_2S(s)$	−79.5	121	−86.2
$CuS(s)$	−53.1	66.5	−53.6
$CuSO_4(s)$	−771.4	109	−661.8
$CuSO_4 \cdot 5H_2O(s)$	−2279.7	300.4	−1879.7
Fluorine			
$F_2(g)$	0	202.7	0
$F^-(aq)$	−332.6	−13.8	−278.8
$HF(g)$	−271	173.5	−273
Gold			
$Au(s)$	0	47.7	0
$Au_2O_3(s)$	+80.8	125	+163
$AuCl_3(s)$	−118	148	−48.5
Hydrogen			
$H_2(g)$	0	130.6	0
$H_2O(l)$	−285.9	69.96	−237.2
$H_2O(g)$	−241.8	188.7	−228.6
$H_2O_2(l)$	−187.6	109.6	−120.3
$H_2Se(g)$	+76	219	+62.3
$H_2Te(g)$	+154	234	+138
Iodine			
$I_2(s)$	0	116.1	0
$I_2(g)$	+62.4	260.7	+19.3
$HI(g)$	+26.6	206	+1.30
Iron			
$Fe(s)$	0	27	0
$Fe^{2+}(aq)$	−89.1	−137.7	−78.9
$Fe^{3+}(aq)$	−48.5	−315.9	−4.7
$Fe_2O_3(s)$	−822.2	90.0	−741.0
$Fe_3O_4(s)$	−1118.4	146.4	−1015.4
$FeS(s)$	−100.0	60.3	−100.4
$FeS_2(s)$	−178.2	52.9	−166.9
Lead			
$Pb(s)$	0	64.8	0
$Pb^{2+}(aq)$	−1.7	10.5	−24.4
$PbCl_2(s)$	−359.4	136	−314.1
$PbO(s)$	−219.2	67.8	−189.3
$PbO_2(s)$	−277	68.6	−219
$Pb(OH)_2(s)$	−515.9	88	−420.9
$PbS(s)$	−100	91.2	−98.7
$PbSO_4(s)$	−920.1	149	−811.3
Lithium			
$Li(s)$	0	28.4	0
$Li^+(aq)$	−278.6	10.3	
$LiF(s)$	−611.7	35.7	−583.3
$LiCl(s)$	−408	59.29	−383.7
$LiBr(s)$	−350.3	66.9	−338.87
$Li_2O(s)$	−596.5	37.9	−560.5
$Li_3N(s)$	−199	37.7	−155.4
Magnesium			
$Mg(s)$	0	32.5	0
$Mg^{2+}(aq)$	−466.9	−138.1	−454.8
$MgCO_3(s)$	−1113	65.7	−1029
$MgF_2(s)$	−1124	79.9	−1056
$MgCl_2(s)$	−641.8	89.5	−592.5
$MgCl_2 \cdot 2H_2O(s)$	−1280	180	−1118
$Mg_3N_2(s)$	−463.2	87.9	−411
$MgO(s)$	−601.7	26.9	−569.4
$Mg(OH)_2(s)$	−924.7	63.1	−833.9

(Continued)

Table C.2 Thermodynamic Data for Selected Elements, Compounds, and Ions (25 °C) *(Continued)*

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	ΔG_f° (kJ mol^{-1})
Manganese			
$Mn(s)$	0	32.0	0
$Mn^{2+}(aq)$	−223	−74.9	−228
$MnO_4^-(aq)$	−542.7	191	−449.4
$KMnO_4(s)$	−813.4	171.71	−713.8
$MnO(s)$	−385	60.2	−363
$Mn_2O_3(s)$	−959.8	110	−882.0
$MnO_2(s)$	−520.9	53.1	−466.1
$Mn_3O_4(s)$	−1387	149	−1280
$MnSO_4(s)$	−1064	112	−956
Mercury			
$Hg(l)$	0	76.1	0
$Hg(g)$	+61.32	175	+31.8
$Hg_2Cl_2(s)$	−265.2	192.5	−210.8
$HgCl_2(s)$	−224.3	146.0	−178.6
$HgO(s)$	−90.83	70.3	−58.54
$HgS(s$, red$)$	−58.2	82.4	−50.6
Nickel			
$Ni(s)$	0	30	0
$NiCl_2(s)$	−305	97.5	−259
$NiO(s)$	−244	38	−216
$NiO_2(s)$			−199
$NiSO_4(s)$	−891.2	77.8	−773.6
$NiCO_3(s)$	−664.0	91.6	−615.0
$Ni(CO)_4(g)$	−220	399	−567.4
Nitrogen			
$N_2(g)$	0	191.5	0
$NH_3(g)$	−46.19	192.5	−16.7
$NH_4^+(aq)$	−132.5	113	−79.37
$N_2H_4(g)$	+95.40	238.4	+159.3
$N_2H_4(l)$	+50.6	121.2	+149.4
$NH_4Cl(s)$	−315.4	94.6	−203.9
$NO(g)$	+90.37	210.6	+86.69
$NO_2(g)$	+33.8	240.5	+51.84
$N_2O(g)$	+81.57	220.0	+103.6
$N_2O_4(g)$	+9.67	304	+98.28
$N_2O_5(g)$	+11	356	+115
$HNO_3(l)$	−173.2	155.6	−79.91
$NO_3^-(aq)$	−205.0	146.4	−108.74
Oxygen			
$O_2(g)$	0	205.0	0
$O_3(g)$	+143	238.8	+163
$OH^-(aq)$	−230.0	−10.75	−157.24
Phosphorus			
$P(s$, white$)$	0	41.09	0
$P_4(g)$	+314.6	163.2	+278.3

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	ΔG_f° (kJ mol^{-1})
$PCl_3(g)$	−287.0	311.8	−267.8
$PCl_5(g)$	−374.9	364.6	−305.0
$PH_3(g)$	+5.4	210.2	+12.9
$P_4O_6(s)$	−1640		
$POCl_3(g)$	−558.5	325.5	−512.9
$POCl_3(l)$	−597.1	222.5	−520.8
$P_4O_{10}(s)$	−2984	228.9	−2698
$H_3PO_4(s)$	−1279	110.5	−1119
Potassium			
$K(s)$	0	64.18	0
$K^+(aq)$	−252.4	102.5	−283.3
$KF(s)$	−567.3	66.6	−537.8
$KCl(s)$	−435.89	82.59	−408.3
$KBr(s)$	−393.8	95.9	−380.7
$KI(s)$	−327.9	106.3	−324.9
$KOH(s)$	−424.8	78.9	−379.1
$K_2O(s)$	−361	98.3	−322
$K_2SO_4(s)$	−1433.7	176	−1316.4
Silicon			
$Si(s)$	0	19	0
$SiH_4(g)$	+33	205	+52.3
$SiO_2(s$, alpha$)$	−910.0	41.8	−856
Silver			
$Ag(s)$	0	42.55	0
$Ag^+(aq)$	+105.58	72.68	+77.11
$AgCl(s)$	−127.0	96.2	−109.7
$AgBr(s)$	−100.4	107.1	−96.9
$AgNO_3(s)$	−124	141	−32
$Ag_2O(s)$	−31.1	121.3	−11.2
Sodium			
$Na(s)$	0	51.0	0
$Na^+(aq)$	−240.12	59.0	−261.91
$NaF(s)$	−571	51.5	−545
$NaCl(s)$	−411.0	72.38	−384.0
$NaBr(s)$	−360	83.7	−349
$NaI(s)$	−288	91.2	−286
$NaHCO_3(s)$	−947.7	102	−851.9
$Na_2CO_3(s)$	−1131	136	−1048
$Na_2O_2(s)$	−510.9	94.6	−447.7
$Na_2O(s)$	−510	72.8	−376
$NaOH(s)$	−426.8	64.18	−382
$Na_2SO_4(s)$	−1384.49	149.49	−1266.83
Sulfur			
$S(s$, rhombic$)$	0	31.9	0
$SO_2(g)$	−296.9	248.5	−300.4
$SO_3(g)$	−395.2	256.2	−370.4

(Continued)

Table C.2 Thermodynamic Data for Selected Elements, Compounds, and Ions (25 °C) *(Continued)*

Substance	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	ΔG_f° (kJ mol^{-1})
$H_2S(g)$	−20.6	206	−33.6
$H_2SO_4(l)$	−811.32	157	−689.9
$H_2SO_4(aq)$	−909.3	20.1	−744.5
$SF_6(g)$	−1209	292	−1105
Tin			
Sn(*s*, white)	0	51.6	0
$Sn^{2+}(aq)$	−8.8	−17	−27.2
$SnCl_4(l)$	−511.3	258.6	−440.2
$SnO(s)$	−285.8	56.5	−256.9
$SnO_2(s)$	−580.7	52.3	−519.6
Zinc			
$Zn(s)$	0	41.6	0
$Zn^{2+}(aq)$	−153.9	−112.1	−147.06
$ZnCl_2(s)$	−415.1	111	−369.4
$ZnO(s)$	−348.3	43.6	−318.3
$ZnS(s)$	−205.6	57.7	−201.3
$ZnSO_4(s)$	−982.8	120	−874.5

Table C.3 Heats of Formation of Gaseous Atoms from Elements in Their Standard States

Element	ΔH_f° (kJ mol^{-1})[a]
Group 1A	
H	217.89
Li	161.5
Na	107.8
K	89.62
Rb	82.0
Cs	78.2
Group 2A	
Be	324.3
Mg	146.4
Ca	178.2
Sr	163.6
Ba	177.8
Group 3A	
B	560
Al	329.7
Group 4A	
C	716.67
Si	450
Group 5A	
N	472.68
P	332.2
Group 6A	
O	249.17
S	276.98
Group 7A	
F	79.14
Cl	121.47
Br	112.38
I	107.48

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[a] All values in this table are positive because forming the gaseous atoms from the elements is endothermic: it involves bond breaking.

Table C.4 Average Bond Energies

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
C—C	348	C—Br	276
C═C	612	C—I	238
C≡C	960	H—H	436
C—H	412	H—F	565
C—N	305	H—Cl	431
C═N	613	H—Br	366
C≡N	890	H—I	299
C—O	360	H—N	388
C═O	743	H—O	463
C—F	484	H—S	338
C—Cl	338	H—Si	376

Table C.5 Vapor Pressure of Water as a Function of Temperature

Temp (°C)	Vapor Pressure (torr)	Temp (°C)	Vapor Pressure (torr)	Temp (°C)	Vapor Pressure (torr)	Temp (°C)	Vapor Pressure (torr)
0	4.58	26	25.2	52	102.1	78	327.3
1	4.93	27	26.7	53	107.2	79	341.0
2	5.29	28	28.3	54	112.5	80	355.1
3	5.68	29	30.0	55	118.0	81	369.7
4	6.10	30	31.8	56	123.8	82	384.9
5	6.54	31	33.7	57	129.8	83	400.6
6	7.01	32	35.7	58	136.1	84	416.8
7	7.51	33	37.7	59	142.6	85	433.6
8	8.04	34	39.9	60	149.4	86	450.9
9	8.61	35	41.2	61	156.4	87	468.7
10	9.21	36	44.6	62	163.8	88	487.1
11	9.84	37	47.1	63	171.4	89	506.1
12	10.5	38	49.7	64	179.3	90	525.8
13	11.2	39	52.4	65	187.5	91	546.0
14	12.0	40	55.3	66	196.1	92	567.0
15	12.8	41	58.3	67	205.0	93	588.6
16	13.6	42	61.5	68	214.2	94	610.9
17	14.5	43	64.8	69	223.7	95	633.9
18	15.5	44	68.3	70	233.7	96	657.6
19	16.5	45	71.9	71	243.9	97	682.1
20	17.5	46	75.6	72	254.6	98	707.3
21	18.7	47	79.6	73	265.7	99	733.2
22	19.8	48	83.7	74	277.2	100	760.0
23	21.1	49	88.0	75	289.1		
24	22.4	50	92.5	76	301.4		
25	23.8	51	97.2	77	314.1		

Table C.6 Solubility Product Constants

Salt	K_{sp}
Fluorides	
MgF_2	5.2×10^{-11}
CaF_2	3.4×10^{-11}
SrF_2	4.3×10^{-9}
BaF_2	1.8×10^{-7}
LiF	1.8×10^{-3}
PbF_2	3.3×10^{-8}
Chlorides	
$CuCl$	1.7×10^{-7}
$AgCl$	1.8×10^{-10}
Hg_2Cl_2	1.4×10^{-18}
$TlCl$	1.9×10^{-4}
$PbCl_2$	1.7×10^{-5}
$AuCl_3$	3.2×10^{-25}
Bromides	
$CuBr$	6.3×10^{-9}
$AgBr$	5.4×10^{-13}
Hg_2Br_2	6.4×10^{-23}
$HgBr_2$	6.2×10^{-20}
$PbBr_2$	6.6×10^{-6}
Iodides	
CuI	1.3×10^{-12}
AgI	8.5×10^{-17}
Hg_2I_2	5.2×10^{-29}
HgI_2	2.9×10^{-29}
PbI_2	9.8×10^{-9}
Hydroxides	
$Mg(OH)_2$	5.6×10^{-12}
$Ca(OH)_2$	5.0×10^{-6}
$Mn(OH)_2$	1.6×10^{-13}
$Fe(OH)_2$	4.9×10^{-17}
$Fe(OH)_3$	2.8×10^{-39}
$Co(OH)_2$	5.9×10^{-15}
$Co(OH)_3$	3×10^{-45}
$Ni(OH)_2$	5.5×10^{-16}
$Cu(OH)_2$	4.8×10^{-20}
$V(OH)_3$	4×10^{-35}
$Cr(OH)_3$	2×10^{-30}
Ag_2O	1.9×10^{-8}
$Zn(OH)_2$	3×10^{-17}
$Cd(OH)_2$	7.2×10^{-15}
$Al(OH)_3$ (alpha form)	3×10^{-34}
Cyanides	
$AgCN$	6.0×10^{-17}
$Zn(CN)_2$	3×10^{-16}
Sulfites	
$CaSO_3 \cdot \frac{1}{2}H_2O$	3.1×10^{-7}
Ag_2SO_3	1.5×10^{-14}
$BaSO_3$	5.0×10^{-10}
Sulfates	
$CaSO_4$	4.9×10^{-5}
$SrSO_4$	3.4×10^{-7}
$BaSO_4$	1.1×10^{-10}
$RaSO_4$	3.7×10^{-11}
Ag_2SO_4	1.2×10^{-5}
Hg_2SO_4	6.5×10^{-7}
$PbSO_4$	2.5×10^{-8}
Chromates	
$BaCrO_4$	1.2×10^{-10}
$CuCrO_4$	3.6×10^{-6}
Ag_2CrO_4	1.1×10^{-12}
Hg_2CrO_4	2.0×10^{-9}
$CaCrO_4$	7.1×10^{-4}
$PbCrO_4$	1.8×10^{-14}
Carbonates	
$MgCO_3$	6.8×10^{-8}
$CaCO_3$	3.4×10^{-9}
$SrCO_3$	5.6×10^{-10}
$BaCO_3$	2.6×10^{-9}
$MnCO_3$	2.2×10^{-11}
$FeCO_3$	3.1×10^{-11}
$CoCO_3$	1.0×10^{-10}
$NiCO_3$	1.4×10^{-7}
$CuCO_3$	2.5×10^{-10}
Ag_2CO_3	8.5×10^{-12}
Hg_2CO_3	3.6×10^{-17}
$ZnCO_3$	1.5×10^{-10}
$CdCO_3$	1.0×10^{-12}
$PbCO_3$	7.4×10^{-14}
Phosphates	
$Ca_3(PO_4)_2$	2.1×10^{-33}
$Mg_3(PO_4)_2$	1.0×10^{-24}
$SrHPO_4$	1.2×10^{-7}
$BaHPO_4$	4.0×10^{-8}
$LaPO_4$	3.7×10^{-23}
$Fe_3(PO_4)_2$	1×10^{-36}
Ag_3PO_4	8.9×10^{-17}
$FePO_4$	9.9×10^{-16}
$Zn_3(PO_4)_2$	5×10^{-36}
$Pb_3(PO_4)_2$	3.0×10^{-44}
$Ba_3(PO_4)_2$	5.8×10^{-38}
Ferrocyanides	
$Zn_2[Fe(CN)_6]$	2.1×10^{-16}
$Cd_2[Fe(CN)_6]$	4.2×10^{-18}
$Pb_2[Fe(CN)_6]$	9.5×10^{-19}

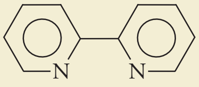
Table C.7 Formation Constants of Complexes (25 °C)

Complex Ion Equilibrium	K_{form}
Halide Complexes	
$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	1×10^{20}
$Al^{3+} + 4F^- \rightleftharpoons [AlF_4]^-$	2.0×10^{8}
$Be^{2+} + 4F^- \rightleftharpoons [BeF_4]^{2-}$	1.3×10^{13}
$Sn^{4+} + 6F^- \rightleftharpoons [SnF_6]^{2-}$	1×10^{25}
$Cu^+ + 2Cl^- \rightleftharpoons [CuCl_2]^-$	3×10^{5}
$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$	1.8×10^{5}
$Pb^{2+} + 4Cl^- \rightleftharpoons [PbCl_4]^{2-}$	2.5×10^{15}
$Zn^{2+} + 4Cl^- \rightleftharpoons [ZnCl_4]^{2-}$	1.6
$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	5.0×10^{15}
$Cu^+ + 2Br^- \rightleftharpoons [CuBr_2]^-$	8×10^{5}
$Ag^+ + 2Br^- \rightleftharpoons [AgBr_2]^-$	1.7×10^{7}
$Hg^{2+} + 4Br^- \rightleftharpoons [HgBr_4]^{2-}$	1×10^{21}
$Cu^+ + 2I^- \rightleftharpoons [CuI_2]^-$	8×10^{8}
$Ag^+ + 2I^- \rightleftharpoons [AgI_2]^-$	1×10^{11}
$Pb^{2+} + 4I^- \rightleftharpoons [PbI_4]^{2-}$	3×10^{4}
$Hg^{2+} + 4I^- \rightleftharpoons [HgI_4]^{2-}$	1.9×10^{30}
Ammonia Complexes	
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^{7}
$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$	7.8×10^{8}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$Hg^{2+} + 4NH_3 \rightleftharpoons [Hg(NH_3)_4]^{2+}$	1.8×10^{19}
$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	5.0×10^{4}
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	4.6×10^{33}
$Cd^{2+} + 6NH_3 \rightleftharpoons [Cd(NH_3)_6]^{2+}$	2.6×10^{5}
$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
Cyanide Complexes	
$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.0×10^{24}
$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1.0×10^{31}
$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	5.3×10^{18}
$Cu^+ + 2CN^- \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}
$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	7.7×10^{16}
$Au^+ + 2CN^- \rightleftharpoons [Au(CN)_2]^-$	2×10^{38}

Complex Ion Equilibrium	K_{form}
Complexes with Other Monodentate Ligands	
Methylamine (CH_3NH_2)	
$Ag^+ + 2CH_3NH_2 \rightleftharpoons [Ag(CH_3NH_2)_2]^+$	7.8×10^{6}
Thiocyanate Ion (SCN^-)	
$Cd^{2+} + 4SCN^- \rightleftharpoons [Cd(SCN)_4]^{2-}$	1×10^{3}
$Cu^{2+} + 2SCN^- \rightleftharpoons [Cu(SCN)_2]$	5.6×10^{3}
$Fe^{3+} + 3SCN^- \rightleftharpoons [Fe(SCN)_3]$	2×10^{6}
$Hg^{2+} + 4SCN^- \rightleftharpoons [Hg(SCN)_4]^{2-}$	5.0×10^{21}
Hydroxide Ion (OH^-)	
$Cu^{2+} + 4OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$	1.3×10^{16}
$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{20}
Complexes with Bidentate Ligands*	
$Mn^{2+} + 3\ en \rightleftharpoons [Mn(en)_3]^{2+}$	6.5×10^{5}
$Fe^{2+} + 3\ en \rightleftharpoons [Fe(en)_3]^{2+}$	5.2×10^{9}
$Co^{2+} + 3\ en \rightleftharpoons [Co(en)_3]^{2+}$	1.3×10^{14}
$Co^{3+} + 3\ en \rightleftharpoons [Co(en)_3]^{3+}$	4.8×10^{48}
$Ni^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+}$	4.1×10^{17}
$Cu^{2+} + 2\ en \rightleftharpoons [Cu(en)_2]^{2+}$	3.5×10^{19}
$Mn^{2+} + 3\ bipy \rightleftharpoons [Mn(bipy)_3]^{2+}$	1×10^{6}
$Fe^{2+} + 3\ bipy \rightleftharpoons [Fe(bipy)_3]^{2+}$	1.6×10^{17}
$Ni^{2+} + 3\ bipy \rightleftharpoons [Ni(bipy)_3]^{2+}$	3.0×10^{20}
$Co^{2+} + 3\ bipy \rightleftharpoons [Co(bipy)_3]^{2+}$	8×10^{15}
$Mn^{2+} + 3\ phen \rightleftharpoons [Mn(phen)_3]^{2+}$	2×10^{10}
$Fe^{2+} + 3\ phen \rightleftharpoons [Fe(phen)_3]^{2+}$	1×10^{21}
$Co^{2+} + 3\ phen \rightleftharpoons [Co(phen)_3]^{2+}$	6×10^{19}
$Ni^{2+} + 3\ phen \rightleftharpoons [Ni(phen)_3]^{2+}$	2×10^{24}
$Co^{2+} + 3C_2O_4^{\ 2-} \rightleftharpoons [Co(C_2O_4)_3]^{4-}$	4.5×10^{6}
$Fe^{3+} + 3C_2O_4^{\ 2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	3.3×10^{20}
Complexes of Other Polydentate Ligands*	
$Zn^{2+} + EDTA^{4-} \rightleftharpoons [Zn(EDTA)]^{2-}$	3.8×10^{16}
$Mg^{2+} + 2NTA^{3-} \rightleftharpoons [Mg(NTA)_2]^{4-}$	1.6×10^{10}
$Ca^{2+} + 2NTA^{3-} \rightleftharpoons [Ca(NTA)_2]^{4-}$	3.2×10^{11}

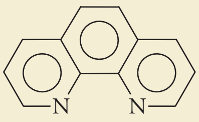
*en = ethylenediamine

bipy = bipyridyl



bipyridyl

phen = 1,10-phenanthroline



1,10-phenanthroline

$EDTA^{4-}$ = ethylenediaminetetraacetate ion

NTA^{3-} = nitrilotriacetate ion

Table C.8 Ionization Constants of Weak Acids and Bases (Alternative Formulas in Parentheses)

Monoprotic Acid	Name	K_a
$HC_2O_2Cl_3$ (Cl_3CCO_2H)	trichloroacetic acid	2.2×10^{-1}
HIO_3	iodic acid	1.7×10^{-1}
$HC_2HO_2Cl_2$ (Cl_2CHCO_2H)	dichloroacetic acid	5.0×10^{-2}
$HC_2H_2O_2Cl$ (ClH_2CCO_2H)	chloroacetic acid	1.4×10^{-3}
HNO_2	nitrous acid	4.6×10^{-4}
HF	hydrofluoric acid	3.5×10^{-4}
HOCN	cyanic acid	2×10^{-4}
$HCHO_2$ (HCO_2H)	formic acid	1.8×10^{-4}
$HC_3H_5O_3$ [$CH_3CH(OH)CO_2H$]	lactic acid	1.4×10^{-4}
$HC_4H_3N_2O_3$	barbituric acid	9.8×10^{-5}
$HC_7H_5O_2$ ($C_6H_5CO_2H$)	benzoic acid	6.3×10^{-5}
$HC_4H_7O_2$ ($CH_3CH_2CH_2CO_2H$)	butanoic acid	1.5×10^{-5}
HN_3	hydrazoic acid	2.5×10^{-5}
$HC_2H_3O_2$ (CH_3CO_2H)	acetic acid	1.8×10^{-5}
$HC_3H_5O_2$ ($CH_3CH_2CO_2H$)	propanoic acid	1.3×10^{-5}
$HC_6H_4NO_2$	nicotinic acid (niacin)	1.4×10^{-5}
HOCl	hypochlorous acid	3.0×10^{-8}
HOBr	hypobromous acid	2.1×10^{-9}
HCN	hydrocyanic acid	4.9×10^{-10}
HC_6H_5O	phenol	1.3×10^{-10}
HOI	hypoiodous acid	2.3×10^{-11}
H_2O_2	hydrogen peroxide	2.4×10^{-12}

Polyprotic Acid	Name	K_{a_1}	K_{a_2}	K_{a_3}
H_2SO_4	sulfuric acid	large	1.2×10^{-2}	
H_2CrO_4	chromic acid	5.0	1.5×10^{-6}	
$H_2C_2O_4$	oxalic acid	6.0×10^{-2}	6.1×10^{-5}	
H_3PO_3	phosphorous acid	5.0×10^{-2}	2.0×10^{-7}	
$H_2S(aq)$	hydrosulfuric acid	8.9×10^{-8}	1×10^{-19}	
H_2SO_3	sulfurous acid	1.2×10^{-2}	6.6×10^{-8}	
H_2SeO_4	selenic acid	large	1.2×10^{-2}	
H_2SeO_3	selenous acid	4.5×10^{-3}	1.1×10^{-8}	
H_6TeO_6	telluric acid	2×10^{-8}	1×10^{-11}	
H_2TeO_3	tellurous acid	3.3×10^{-3}	2.0×10^{-8}	
$H_2C_3H_2O_4$ ($HO_2CCH_2CO_2H$)	malonic acid	1.4×10^{-3}	2.0×10^{-6}	
$H_2C_8H_4O_4$	phthalic acid	1.1×10^{-3}	3.9×10^{-6}	
$H_2C_4H_4O_6$	tartaric acid	9.2×10^{-4}	4.3×10^{-5}	
$H_2C_6H_6O_6$	ascorbic acid	8.0×10^{-5}	1.6×10^{-12}	
H_2CO_3	carbonic acid	4.3×10^{-7}	5.6×10^{-11}	
H_3PO_4	phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
H_3AsO_4	arsenic acid	5.5×10^{-3}	1.7×10^{-7}	5.1×10^{-12}
$H_3C_6H_5O_7$	citric acid	7.1×10^{-4}	1.7×10^{-5}	6.3×10^{-6}

(*Continued*)

Table C.8 Ionization Constants of Weak Acids and Bases (Alternative Formulas in Parentheses) *(Continued)*

Weak Base	Name	K_b
$(CH_3)_2NH$	dimethylamine	9.6×10^{-4}
$C_4H_9NH_2$	butylamine	5.9×10^{-4}
CH_3NH_2	methylamine	4.4×10^{-4}
$CH_3CH_2NH_2$	ethylamine	4.3×10^{-4}
$(CH_3)_3N$	trimethylamine	7.4×10^{-5}
NH_3	ammonia	1.8×10^{-5}
$C_{21}H_{22}N_2O_2$	strychnine	1.8×10^{-6}
N_2H_4	hydrazine	1.3×10^{-6}
$C_{17}H_{19}NO_3$	morphine	1.6×10^{-6}
NH_2OH	hydroxylamine	1.1×10^{-8}
C_5H_5N	pyridine	1.7×10^{-9}
$C_6H_5NH_2$	aniline	3.9×10^{-10}
PH_3	phosphine	10^{-28}

Table C.9 Standard Reduction Potentials (25 °C)

$E°$ (Volts)	Half-Cell Reaction
+2.87	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$
+2.08	$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O$
+2.01	$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$
+1.82	$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$
+1.77	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O$
+1.695	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$
+1.69	$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$
+1.63	$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$
+1.51	$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$
+1.46	$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$
+1.44	$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$
+1.42	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$
+1.36	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O$
+1.24	$O_3(g) + H_2O + 2e^- \rightleftharpoons O_2(g) + 2OH^-(aq)$
+1.23	$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$
+1.20	$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s)$
+1.07	$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O$
+0.94	$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons HNO_2(aq) + H_2O$
+0.91	$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$
+0.87	$HO_2^-(aq) + H_2O + 2e^- \rightleftharpoons 3OH^-(aq)$
+0.80	$NO_3^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons 2NO_2(g) + 2H_2O$
+0.80	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$
+0.69	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$
+0.54	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$
+0.49	$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$
+0.45	$SO_2(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 2H_2O$
+0.401	$O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
+0.27	$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$
+0.25	$PbO_2(s) + H_2O + 2e^- \rightleftharpoons PbO(s) + 2OH^-(aq)$
+0.2223	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$
+0.172	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$
+0.169	$S_4O_6^{2-}(aq) + 2e^- \rightleftharpoons 2S_2O_3^{2-}(aq)$
+0.16	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$
+0.15	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$
+0.14	$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$
+0.07	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$
0 (exactly)	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$
−0.13	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$

(Continued)

Table C.9 Standard Reduction Potentials (25 °C) *(Continued)*

E° (Volts)	Half-Cell Reaction
−0.14	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$
−0.15	$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-(aq)$
−0.25	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$
−0.28	$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$
−0.34	$In^{3+}(aq) + 3e^- \rightleftharpoons In(s)$
−0.34	$Tl^+(aq) + e^- \rightleftharpoons Tl(s)$
−0.36	$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$
−0.40	$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$
−0.56	$Ga^{3+}(aq) + 3e^- \rightleftharpoons Ga(s)$
−0.58	$PbO(s) + H_2O + 2e^- \rightleftharpoons Pb(s) + 2OH^-(aq)$
−0.74	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
−0.81	$Cd(OH)_2(s) + 2e^- \rightleftharpoons Cd(s) + 2OH^-(aq)$
−0.83	$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$
−0.88	$Fe(OH)_2(s) + 2e^- \rightleftharpoons Fe(s) + 2OH^-(aq)$
−0.91	$Cr^{2+}(aq) + 2e^- \rightleftharpoons Cr(s)$
−1.16	$N_2(g) + 4H_2O + 4e^- \rightleftharpoons N_2O_4(aq) + 4OH^-(aq)$
−1.18	$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$
−1.216	$ZnO_2^-(aq) + 2H_2O + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq)$
−1.63	$Ti^{2+}(aq) + 2e^- \rightleftharpoons Ti(s)$
−1.66	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$
−1.79	$U^{3+}(aq) + 3e^- \rightleftharpoons U(s)$
−2.02	$Sc^{3+}(aq) + 3e^- \rightleftharpoons Sc(s)$
−2.36	$La^{3+}(aq) + 3e^- \rightleftharpoons La(s)$
−2.37	$Y^{3+}(aq) + 3e^- \rightleftharpoons Y(s)$
−2.37	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$
−2.71	$Na^+(aq) + e^- \rightleftharpoons Na(s)$
−2.76	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$
−2.89	$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$
−2.90	$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$
−2.92	$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$
−2.92	$K^+(aq) + e^- \rightleftharpoons K(s)$
−2.93	$Rb^+(aq) + e^- \rightleftharpoons Rb(s)$
−3.05	$Li^+(aq) + e^- \rightleftharpoons Li(s)$

Glossary

This glossary has the definitions of the key terms that were marked in boldface throughout the chapters plus a few additional terms. The numbers in parentheses that follow the definitions are the numbers of the sections in which the glossary entries received their principal discussions.

A

Abbreviated Electron Configurations: A shorthand method to write electron configurations using the preceding noble gase to represent core electrons. (8.8)

Absolute Zero: 0 K, −273.15 °C. Nature's lowest temperature. (2.2, 11.3)

Acceptor: A Lewis acid; the central metal ion in a complex ion. (18.4, 22.1)

Accuracy: The closeness of a measurement to the true value. (2.3)

Acid: *Arrhenius definition:* A substance that produces hydronium ions (hydrogen ions) in water. (5.3)
Brønsted definition: A proton donor. (16.1)
Lewis definition: An electron-pair acceptor. (16.4)

Acid Anhydride: Generally, an oxide of a nonmetal. (5.3)

Acid–Base Indicator: A dye with one color in acid and another color in base. (5.3, 5.8)

Acid–Base Neutralization: The reaction of an acid with a base. (5.3, 16.4)

Acid Ionization Constant (K_a):

$$K_a = \frac{[H^+][A^-]}{[HA]} \text{ for the equilibrium,}$$

$$HA \rightleftharpoons H^+ + A^- \qquad (17.3)$$

Acid Rain: Rain made acidic by dissolving sulfur and nitrogen oxides from the atmosphere.

Acid Salt: A salt of a partially neutralized polyprotic acid, for example, $NaHSO_4$ or $NaHCO_3$. (5.4)

Acid Solubility Product: The special solubility product expression for metal sulfides in dilute acid and related to the equation for their dissolving. For a divalent metal sulfide, MS,

$$MS(s) + 2H^+(aq) \rightleftharpoons M^{2+}(aq) + H_2S(aq)$$

$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H^+]^2} \qquad (18.2)$$

Acidic Anhydride: An oxide that reacts with water to make the solution acidic. (5.3)

Acidic Solution: An aqueous solution in which $[H^+] > [OH^-]$. (7.1)

Actinide Elements (Actinide Series): Elements 90–103. (3.2)

Activated Complex: The chemical species that exists with partly broken and partly formed bonds in the transition state. (14.6)

Activation Energy (E_a): The minimum kinetic energy that must be possessed by the reactants in order to result in an effective collision (one that produces products). (14.5)

Activities: Effective concentrations which properly should be substituted into a mass action expression to satisfy the equilibrium law. The activity of a solid is defined as having a value of 1. (15.4)

Activity: For a radioactive material, the number of disintegrations per second. (21.6)

Activity Series: A list of metals in order of their reactivity as reducing agents. (6.4)

Actual Yield: See *Yield, Actual.*

Addition Compound: A molecule formed by the joining of two simpler molecules through formation of a covalent bond (usually a coordinate covalent bond). (9.8)

Addition Polymer: A polymer formed by the simple addition of one monomer unit to another, a process that continues over and over until a very long chain of monomer units is produced. (23.5)

Addition Reaction: The addition of a molecule to a double or triple bond. (23.2)

Adiabatic Change: A change within a system during which no energy enters or leaves the system. (7.3, 19.1)

Aerogel: A modern ceramic that is extremely porous and has a low density (16.6)

Alcohol: An organic compound whose molecules have the —OH group attached to tetrahedral carbon. (3.6, 9.6, 22.3)

Aldehyde: An organic compound whose molecules have the —OH group. (9.6)

Alkali Metals: The Group 1A elements (except hydrogen)—lithium, sodium, potassium, rubidium, cesium, and francium. (3.2)

Alkaline Battery (Alkaline Dry Cell): A zinc–manganese dioxide galvanic cell of 1.54 V used commonly in flashlight batteries. (20.6)

Alkaline Earth Metals: The Group 2A elements—beryllium, magnesium, calcium, strontium, barium, and radium. (3.2)

Alkane: A hydrocarbon whose molecules have only single bonds. (3.6, 23.2)

Alkene: A hydrocarbon whose molecules have one or more double bonds. (23.2)

Alkyl Group: An organic group of carbon and hydrogen atoms related to an alkane but with one less hydrogen atom (e.g., CH_3—, methyl; CH_3CH_2—, ethyl). (16.6, 23.2)

Alkyne: A hydrocarbon whose molecules have one or more triple bonds. (23.2)

Allotrope: One of two or more forms of an element. (10.10)

Allotropy: The existence of an element in two or more molecular or crystalline forms called allotropes. (10.10)

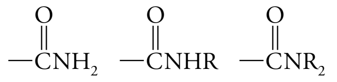
Alpha Particle: The nucleus of a helium atom. (22.3)

Alpha Radiation: A high-velocity stream of alpha particles produced by radioactive decay. (21.3)

Alum: A double salt with the general formula $M^+M^{3+}(SO_4)_2 \cdot 12H_2O$, such as potassium alum: $KAl(SO_4)_2 \cdot 12H_2O$.

Amalgam: A solution of a metal in mercury.

Amide: An organic compound whose molecules have any one of the following groups: (23.4)



$$\text{—}\overset{\overset{\displaystyle O}{\|}}{C}NH_2 \quad \text{—}\overset{\overset{\displaystyle O}{\|}}{C}NHR \quad \text{—}\overset{\overset{\displaystyle O}{\|}}{C}NR_2$$

α-Amino Acid: One of about 20 monomers of polypeptides. (23.6)

Amine: An organic compound whose molecules contain the group NH_2, NHR, or NR_2. (9.6, 23.4)

Amorphous Solid: A noncrystalline solid. A glass. (12.11)

Ampere (A): The SI unit for electric current; one coulomb per second. (20.8)

Amphiprotic Compound: A compound that can act either as a proton donor or as a proton acceptor; an amphoteric compound. (16.1)

Amphoteric Compound: A compound that can react as either an acid or a base. (16.1)

Amplitude: The height of a wave, which is a measure of the wave's intensity. (8.1)

amu: See *Atomic Mass Unit.*

Angstrom (Å): 1 Å = 10^{-10} m = 100 pm = 0.1 nm. (8.10)

Anhydrous: Without water. (1.5)

Anion: A negatively charged ion. (3.4)

Anode: The positive electrode in a gas discharge tube. The electrode at which oxidation occurs during an electrochemical change. (3.1, 20.1)

Antibonding Electrons: Electrons that occupy antibonding molecular orbitals. (10.7)

Antibonding Molecular Orbital: A molecular orbital that denies electron density to the space between nuclei and destabilizes a molecule when occupied by electrons. (10.7)

Antimatter: Any particle annihilated by a particle of ordinary matter. (22.3)

Aqua Regia: One part concentrated nitric acid and three parts concentrated hydrochloric acid (by volume).

Aqueous Solution: A solution that has water as the solvent.

Aromatic Compound: An organic compound whose molecules have the benzene ring system. (23.2)

Aromatic Hydrocarbon: Hydrocarbons that contain a benzene ring or similar ring systems with alternating single and double bonds. (23.2)

Arrhenius Acid: See *Acid*.

Arrhenius Base: See *Base*.

Arrhenius Equation: An equation that relates the rate constant of a reaction to the reaction's activation energy. (14.7)

Association: The joining together of molecules by hydrogen bonds. (13.7)

Asymmetric Carbon Atom: A carbon atom that is bonded to four different groups and which is a chiral center. (23.1)

Atmosphere, Standard (atm): 101,325 Pa. The pressure that supports a column of mercury 760 mm high at 0 °C; 760 torr. (7.5, 11.2)

Atmospheric Pressure: The pressure exerted by the mixture of gases in our atmosphere. (7.5, 11.2)

Atom: A neutral particle having one nucleus; the smallest representative sample of an element. (1.2)

Atomic force microscope: A modern instrument that determines the topology of materials with a resolution on the order of atomic dimensions. Orientations of atoms and structures of molecular assemblies on these surfaces can be deduced from these measurements. (1.6)

Atomic Mass: The average mass (in u) of the atoms of the isotopes of a given element as they occur naturally. (3.1)

Atomic Mass Unit (u): $1.6605402 \times 10^{-24}$ g; 1/12th the mass of one atom of carbon-12. Sometimes given the symbol amu. (3.1)

Atomic Number: The number of protons in a nucleus. (3.1)

Atomic Radiation: Radiation consisting of particles or electromagnetic radiation given off by radioactive elements. (21.3)

Atomic Spectrum: The line spectrum produced when energized or excited atoms emit electromagnetic radiation. (8.2)

Atomic Weight: See *Atomic Mass*.

Atomization Energy (ΔH_{atom}): The energy needed to rupture all of the bonds in one mole of a substance in the gas state and produce its atoms, also in the gas state. (19.10)

Aufbau Principle: A set of rules enabling the construction of an electron structure of an atom from its atomic number. (8.7)

Average: See *Mean*.

Average Bond Order: The bond order of two or more equivalent bonds, determined by dividing the total number of sigma and pi bonds by the number of bonding electron domains. (9.9)

Avogadro's Number (Avogadro's Constant): 6.022×10^{23}; the number of particles or formula units in one mole. (4.1)

Avogadro's Principle: Equal volumes of gases contain equal numbers of molecules when they are at identical temperatures and pressures. (11.4)

Axial Bonds: Covalent bonds oriented parallel to the vertical axis in a trigonal bipyramidal molecule. (10.1)

Azimuthal Quantum Number: The quantum number. (8.5) (See also *Secondary Quantum Number*.)

B

Backbone (Polymer): The long chain of atoms in a polymer to which other groups are attached. (23.5)

Background Radiation: The atomic radiation from the natural radionuclides in the environment and from cosmic radiation. (21.6)

Balance: An apparatus for measuring mass. (2.2)

Balanced Equation: A chemical equation that has on opposites sides of the arrow the same number of each atom and the same net charge. (1.6, 4.4)

Ball and Stick Model: The representation of molecules using colored balls for atoms and sticks representing bonds. (1.5)

Band Gap: The energy difference between the valence band and the conduction band. (10.9)

Band Theory: A theory used to explain electron conduction in metals, semiconductors and insulators. (10.9)

Band of Stability: The envelope that encloses just the stable nuclides in a plot of all nuclides constructed according to their numbers of neutrons versus their numbers of protons. (21.4)

Bar: The standard pressure for thermodynamic quantities; 1 bar = 105 pascals, 1 atm = 101,325 Pa. (7.5, 11.2, 19.5)

Barometer: An apparatus for measuring atmospheric pressure. (11.2)

Base: *Arrhenius theory:* A substance that releases OH^- ions in water. (5.3)
Brønsted theory: A proton acceptor. (16.1)
Lewis theory: An electron-pair acceptor. (16.3)

Base Anhydride: Oxides of metals that when dissolved in water produce a basic solution (5.3)

Base Ionization Constant, K_b:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \text{ for the equilibrium,}$$

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad (17.3)$$

Base Units: The units of the fundamental measurements of the SI. (2.2)

Basic Anhydride: An oxide that can neutralize acid or that reacts with water to give OH^-. (5.3)

Basic Solution: An aqueous solution in which $[H^+] < [OH^-]$. (17.1)

Battery: One or more galvanic cells arranged to serve as a practical source of electricity. (20.6)

Becquerel (Bq): 1 disintegration s^{-1}. The SI unit for the activity of a radioactive source. (21.6)

Bent Molecule (V-Shaped Molecule): A molecule that is nonlinear. (10.2)

Beta Particle: An electron emitted by radioactive decay. (22.3)

Beta Radiation: A stream of electrons produced by radioactive decay. (22.3)

Bidentate Ligand: A ligand that has two atoms that can become simultaneously attached to the same metal ion. (22.1)

Bimolecular Collision: A collision of two molecules. (14.8)

Binary Acid: An acid with the general formula H_nX, where X is a nonmetal. (5.4, 16.3)

Binary Compound: A compound composed of two different elements. (3.4)

Binding Energy, Nuclear: The energy equivalent of the difference in mass between an atomic nucleus and the sum of the masses of its nucleons. (21.2)

Biochemistry: The study of the organic substances in organisms. (3.6, 23.6)

Biological Catalyst: Biological molecule such as an enzyme that catalyzes a chemical reaction.

Black Phosphorus: An allotrope of phosphorus that has a layered structure. (10.10)

Body-Centered Cubic (bcc) Unit Cell: A unit cell having identical atoms, molecules, or ions at the corners of a cube plus one more particle in the center of the cube. (12.11)

Boiling Point: The temperature at which the vapor pressure of the liquid equals the atmospheric pressure. (12.6)

Boiling Point Elevation: A colligative property of a solution by which the solution's boiling point is higher than that of the pure solvent. (13.7)

Bond Angle: The angle formed by two bonds that extend from the same atom. (10.1)

Bond Dipole: A dipole within a molecule associated with a specific bond. (10.3)

Bond Dissociation Energy: See *Bond Energy*.

Bond Distance: See *Bond Length*.

Bond Energy: The energy needed to break one mole of a particular bond to give electrically neutral fragments. (9.5, 19.10)

Bond Length: The distance between two nuclei that are held together by a chemical bond. (9.5)

Bond Order: The number of electron pairs shared between two atoms. The *net* number of pairs of bonding electrons. (9.8)

$$\text{Bond order} = 1/2 \times (\text{no. of bonding } e^- - \text{no. of antibonding } e^-)$$

Bonding Domain: A region between two atoms that contains one or more electron pairs in bonds and that influences molecular shape. (10.2)

Bonding Electrons: Electrons that occupy bonding molecular orbitals. (10.7)

Bonding Molecular Orbital: A molecular orbital that introduces a buildup of electron density between nuclei and stabilizes a molecule when occupied by electrons. (10.7)

Born-Haber Cycle: A method for visualizing energy contributions to a physical or chemical change such as the dissolution of a compound in a solvent or the formation of a compound. (9.2)

Boundary: The interface between a system and its surroundings across which energy or matter might pass. (7.3)

Boyle's Law: See *Pressure–Volume Law*.

Bragg Equation: $n\lambda = 2d \sin \theta$. The equation used to convert X-ray diffraction data into a crystal structure. (12.12)

Branched-Chain Compound: An organic compound in whose molecules the carbon atoms do not all occur one after another in a continuous sequence. (23.1)

Branching (Polymer): The formation of side chains (branches) along the main backbone of a polymer. (23.5)

Branching Step: A step in a chain reaction that produces more chain-propagating species than it consumes. (Chemistry Outside the Classroom 14.1)

Brine: An aqueous solution of sodium chloride, often with other salts. (20.9)

Brønsted Acid: See *Acid*.

Brønsted Base: See *Base*.

Brownian Motion: The random, erratic motions of colloidally dispersed particles in a fluid. (3.6)

Buckminsterfullerene: The C-60 molecule. Also called buckyball. (10.10)

Buckyball: See *Buckminsterfullerene*.

Buffer: (a) A pair of solutes, a conjugate weak acid–weak base pair, that can keep the pH of a solution almost constant if either acid or base is added. (b) A solution containing such a pair of solutes. (17.7)

Buffer Capacity: A measure of how much strong acid or strong base is needed to change the pH of a buffer by some specified amount. (17.7)

Buret: A long tube of glass usually marked in mL and 0.1 mL units and equipped with a stopcock for the controlled addition of a liquid to a receiving flask. (5.8)

By-product: The substances formed by side reactions. (4.6)

C

Calorie (cal): 4.184 J. The energy that will raise the temperature of 1.00 g of water from 14.5 to 15.5 °C. (The nutritional *Calorie*, with a capital C, means 1000 cal or 1 kcal.) (7.1)

Calorimeter: An apparatus used in the determination of the heat of a reaction. (7.5)

Calorimetry: The science of measuring the quantities of heat that are involved in a chemical or physical change. (7.5)

Carbohydrates: Polyhydroxyaldehydes or polyhydroxyketones or substances that yield these by hydrolysis and that are obtained from plants or animals. (23.6)

Carbon Nanotube: Tubular carbon molecules that can be visualized as rolled up sheets of graphite (with hexagonal rings of carbon atoms) capped at each end by half of a spherical fullerene molecule. (10.10)

Carbon Ring: A series of carbon atoms arranged in a ring. (23.1)

Carbonyl Group: An organic functional group consisting of a carbon atom joined to an oxygen atom by a double bond; $C{=}O$. (9.6, 23.3)

Carboxyl Group: The organic functional group of an acid consisting of a carbon joined to an oxygen atom with a double bond and an OH group; $—CO_2H$ or $—COOH$. (9.6, 23.3)

Carboxylic Acid: An organic compound whose molecules have the carboxyl group (9.6, 23.3)

Catalysis: Rate enhancement caused by a catalyst. (14.9)

Catalyst: A substance that in relatively small proportion accelerates the rate of a reaction without being permanently chemically changed. (14.9)

Catenation: The linking together of atoms of the same element to form chains.

Cathode: The negative electrode in a gas discharge tube. The electrode at which reduction occurs during an electrochemical change. (3.1, 20.1)

Cathode Ray: A stream of electrons ejected from a hot metal and accelerated toward a positively charged site in a vacuum tube. (3.1)

Cation: A positively charged ion. (3.4)

Cell Potential, E_{cell}: The potential (voltage) of a galvanic cell when no current is drawn from the cell. (20.2)

Cell Reaction: The overall chemical change that takes place in an electrolytic cell or a galvanic cell. (20.1)

Celsius Scale: A temperature scale on which water freezes at 0 °C and boils at 100 °C (at 1 atm) and that has 100 divisions called Celsius degrees between those two points. (2.2)

Centimeter (cm): 0.01 m. (2.2)

Chain-Growth Polymer: See *Addition Polymer*.

Chain Reaction: A self-sustaining change in which the products of one event cause one or more new events. (Chemistry Outside the Classroom. 14.1)

Change of State: Transformation of matter from one physical state to another. In thermochemistry, any change in a variable used to define the state of a particular system—a change in composition, pressure, volume, or temperature. (12.4)

Charles' Law: See *Temperature–Volume Law*.

Chelate: A complex ion containing rings formed by polydentate ligands. (22.1)

Chelate Effect: The extra stability found in complexes that contain chelate rings. (22.1)

Chemical Bond: The force of electrical attraction that holds atoms together in compounds. (3.6, 9 Introduction)

Chemical Change: A change that converts substances into other substances; a chemical reaction. (1.3)

Chemical Energy: The potential energy of chemicals that is transferred during chemical reactions. (7.1)

Chemical Equation: A before-and-after description that uses formulas and coefficients to represent a chemical reaction. (1.6)

Chemical Equilibrium: Dynamic equilibrium in a chemical system. (5.3, 15.1)

Chemical Formula: A formula written using chemical symbols and subscripts that describes the composition of a chemical compound or element. (1.5)

Chemical Kinetics: The study of rates of reaction. (14 Introduction)

Chemical Property: The ability of a substance, either by itself or with other substances, to undergo a change into new substances. (2.1)

Chemical Reaction: A change in which new substances (products) form from starting materials (reactants). (1.3)

Chemical Symbol: A formula for an element. (1.3)

Chemical Thermodynamics: See *Thermodynamics.*

Chemistry: The study of the compositions of substances and the ways by which their properties are related to their compositions. (1.1)

Chirality: The "handedness" of an object; the property of an object (like a molecule) that makes it unable to be superimposed onto a model of its own mirror image. (22.4)

Cis Isomer: A stereoisomer whose uniqueness is in having two groups on the same side of some reference plane. (22.4)

Clausius–Clapeyron Equation: The relationship between the vapor pressure, the temperature, and the molar heat of vaporization of a substance (where C is a constant). (12.8)

$$\ln P = \frac{\Delta H_{\text{vap}}}{RT} + C$$

Closed-End Manometer: See *Manometer.*

Closed System: A system that can absorb or release energy but not mass across the boundary between the system and its surroundings. (7.3)

Closest-Packed Structure: A crystal structure in which atoms or molecules are packed as efficiently as possible. (12.11)

Codon: An individual unit of hereditary instruction that consists of three, side by side, side chains on a molecule of mRNA. (23.7)

Coefficients: Numbers in front of formulas in chemical equations. (1.6)

Coinage Metals: Copper, silver, and gold.

Collapsing Atom Paradox: The paradox faced by classical physics that predicts a moving electron in an atom should emit energy and spiral into the nucleus. (8 Introduction)

Colligative Property: A property such as vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure whose physical value depends only on the ratio of the numbers of moles of solute and solvent particles and not on their chemical identities. (13.7)

Collision Theory: The rate of a reaction is proportional to the number of effective collisions that occur each second between the reactants. (14.5)

Colloid: Particles with at least one dimension between 1 and 100 nm suspended in a solvent. (13.8)

Combined Gas Law: See *Gas Law, Combined.*

Combustion: A rapid reaction with oxygen accompanied by a flame and the evolution of heat and light. (6.5)

Combustion Analysis: A method for obtaining percentage composition data for organic compounds. (4.3)

Common Ion: The ion in a mixture of ionic substances that is common to the formulas of at least two. (17.7)

Common Ion Effect: The solubility of one salt is reduced by the presence of another having a common ion. (17.7)

Competing Reaction: A reaction that reduces the yield of the main product by forming by-products. (4.6)

Complementary Colors: Two colors, when mixed, result in a neutral color such as gray, black or white. (22.5)

Complex Ion (Complex): The combination of one or more anions or neutral molecules (ligands) with a metal ion. (15.6, 18.4, 22.1)

Compound: A substance consisting of chemically combined atoms from two or more elements and present in a definite ratio. (1.3)

Compound Nucleus: An atomic nucleus carrying excess energy following its capture of some bombarding particle. (21.5)

Compressibility: Capable of undergoing a reduction in volume under increasing pressure. (11.1, 12.3)

Concentrated Solution: A solution that has a large ratio of the amounts of solute to solvent. (5.1)

Concentration: The ratio of the quantity of solute to the quantity of solution (or the quantity of solvent). (5.1) (See *Molal Concentration, Molar Concentration, Mole Fraction, Percentage Concentration.*)

Concentration Table: A part of the strategy for organizing data needed to make certain calculations, particularly any involving equilibria. (15.7)

Conclusion: A statement that is based on what we think about a series of observations. (1.2)

Condensation: The change of a vapor to its liquid or solid state. (12.4)

Condensation Polymer (Step-Growth Polymer): A polymer formed from monomers by splitting out a small molecule such as H_2O or CH_3OH. (23.5)

Condensation Polymerization: The process of forming a condensation polymer. (23.5)

Condensed Formula: Generally a formula of an organic compound written to show the sequence of carbon atoms and functional groups without individual bonds. (9.6, 23.1)

Condensed Structural Formulas (Condensed Structures): See *Condensed Formula.*

Conduction Band: In band theory, this consists of any band of atomic energy levels that is continuous throughout the solid and empty or partially filled with electrons. (10.9)

Conformation: A particular relative orientation or geometric form of a flexible molecule. (10.5)

Conjugate Acid: The species in a conjugate acid–base pair that has the greater number of H-units. (16.1)

Conjugate Acid–Base Pair: Two substances (ions or molecules) whose formulas differ by only one H-unit. (16.1)

Conjugate Base: The species in a conjugate acid–base pair that has the fewer number of H-units. (16.1)

Conservation of Energy, Law of: See *Law of Conservation of Energy.*

Conservation of Mass–Energy, Law of: See *Law of Conservation of Mass–Energy.*

Continuous Spectrum: The electromagnetic spectrum corresponding to the mixture of frequencies present in white light. (8.2)

Contributing Structure: One of a set of two or more Lewis structures used in applying the theory of resonance to the structure of a compound. A resonance structure. (9.9)

Conversion Factor: A ratio constructed from the relationship between two units such as 2.54 cm/1 in., from 1 in. = 2.54 cm. (2.4)

Cooling Curve: A graph showing how the temperature of a substance changes as heat is removed from it at a constant rate as the substance undergoes changes in its physical state. (12.7)

Coordinate Covalent Bond: A covalent bond in which both electrons originated from one of the joined atoms, but otherwise like a covalent bond in all respects. (9.8)

Coordination Compound (Coordination Complex): A complex or its salt. (19.4, 22.1)

Coordination Number: The number of donor atoms that surround a metal ion. (22.3)

Copolymer: A polymer made from two or more different monomers. (22.6)

Core Electrons: The inner electrons of an atom that are not exposed to the electrons of other atoms when chemical bonds form. (8.10)

Corrosion: The slow oxidation of metals exposed to air or water. (6.5)

Coulomb (C): The SI unit of electrical charge; the charge on 6.25×10^{18} electrons; the amount of charge that passes a fixed point of a wire conductor when a current of 1 A flows for 1 s. (20.2)

Coulomb's Law: This is the mathematical equation that describes the attractive and repulsive forces between charged particles. (9.2)

Counter Ions: Ions present in a system to assure that the overall charge is zero. (22.1)

Covalent Bond: A chemical bond that results when atoms share electron pairs. (9.5)

Covalent Crystal (Network Solid): A crystal in which the lattice positions are occupied by atoms that are covalently bonded to the atoms at adjacent lattice sites. (12.13)

Critical Mass: The mass of a fissile isotope above which a self-sustaining chain reaction occurs. (21.8)

Critical Point: The point at the end of a vapor pressure versus temperature curve for a liquid and that corresponds to the critical pressure and the critical temperature. (12.10)

Critical Pressure (P_c): The vapor pressure of a substance at its critical temperature. (12.10)

Critical Temperature (T_c): The temperature above which a substance cannot exist as a liquid regardless of the pressure. (12.10)

Crystal Field Splitting (Δ): The difference in energy between sets of *d* orbitals in a complex ion. (22.5)

Crystal Field Theory: A theory that considers the effects of the polarities or the charges of the ligands in a complex ion on the energies of the *d* orbitals of the central metal ion. (22.5)

Crystal Lattice: The repeating symmetrical pattern of atoms, molecules, or ions that occurs in a crystal. (12.11)

Cubic Closest Packing (ccp): Efficient packing of spheres with an A-B-C-A-B-C . . . alternating stacking of layers of spheres. (12.11)

Cubic Meter (m^3): The SI derived unit of volume. (2.2)

Curie (Ci): A unit of activity for radioactive samples, equal to 3.7×10^{10} disintegrations per second. (21.6)

D

Dalton: One atomic mass unit, u.

Dalton's Atomic Theory: Matter consists of tiny, indestructible particles called atoms. All atoms of one element are identical. The atoms of different elements have different masses. Atoms combine in definite ratios by atoms when they form compounds. (1.4)

Dalton's Law of Partial Pressures: See *Partial Pressures, Law of.*

Data: The information (often in the form of physical quantities) obtained in an experiment or other experience or from references. (1.2)

Debye: Unit used to express dipole moments. $1\ \text{D} \times 3.34 \times 10^{-30}\ \text{C m}$ (coulomb meter). (9.7)

Decay Constant: The first-order rate constant for radioactive decay. (21.6)

Decimal Multipliers: Factors—exponentials of 10 or decimals—that are used to define larger or smaller SI units. (2.2)

Decomposition: A chemical reaction that changes one substance into two or more simpler substances. (1.3)

Dehydration: Removal of water from a substance. (23.3)

Dehydration Reaction: Formation of a carbon–carbon double bond by removal of the components of water from an alcohol. (23.3)

Deliquescent Compound: A compound able to absorb enough water from humid air to form a concentrated solution.

Delocalization Energy: The difference between the energy a substance would have if its molecules had no delocalized molecular orbitals and the energy it has because of such orbitals. (10.8)

Delocalized Molecular Orbital: A molecular orbital that spreads over more than two nuclei. (10.8)

ΔH_{fusion}: See *Molar Heat of Fusion*

$\Delta H_{\text{sublimation}}$: See *Molar Heat of Sublimation*

$\Delta H_{\text{vaporization}}$: See *Molar Heat of Vaporization*

Density: The ratio of an object's mass to its volume. (2.5)

Dependent Variable: The experimental variable of a pair of variables whose value is determined by the other, the independent variable.

Deposition: The term describing the opposite of sublimation. (12.4)

Derived Unit: Any unit defined solely in terms of base units. (2.2)

Deuterium: The isotope of hydrogen with a mass number of 2. (21.8)

Diagonal Trend: Physical or chemical properties that generally vary diagonally from one corner to the other in the periodic table (e.g., ionization energy, electron affinity, and electronegativity). (8.10)

Dialysis: The passage of small molecules and ions, but not species of a colloidal size, through a semipermeable membrane. (13.7)

Dialyzing membrane: A membrane that allows the passage of solvent and small solutes through its pores, but large molecules cannot pass through the pores. (13.7)

Diamagnetism: The property experienced by a substance that contains no unpaired electrons whereby the substance is repelled weakly by a magnet. (8.6)

Diamond: A crystalline form of carbon in which each carbon atom is bonded in a tetrahedral structure to four other carbon atoms. (10.10)

Diaphragm Cell: An electrolytic cell used to manufacture sodium hydroxide by the electrolysis of aqueous sodium chloride. (20.9)

Diatomic Substance (Diatomic Molecule): A molecular substance made from two atoms. (1.5)

Diffraction: Constructive and destructive interference by waves. (8.4)

Diffraction Pattern: The image formed on a screen or a photographic film caused by the diffraction of electromagnetic radiation such as visible light or X rays. (12.12)

Diffusion: The spontaneous intermingling of one substance with another. (11.6)

Dilute Solution: A solution in which the ratio of the quantities of solute to solvent is small. (5.1)

Dilution: The process whereby a concentrated solution is made more dilute. (4.6)

Dimensional Analysis: A method for converting one set of units to another that relies on a logical sequence of steps and unit cancellation. (2.4)

Dimer: Two monomer units joined by chemical bonds or intramolecular forces. (13.7)

Dipole (Electric): Partial positive and partial negative charges separated by a distance. (9.7, 12.2)

Dipole–Dipole Attraction: Attraction between molecules that are dipoles. (12.2)

Dipole Moment (μ): The product of the sizes of the partial charges in a dipole multiplied by the distance between them; a measure of the polarity of a molecule. (9.7)

Diprotic Acid: An acid that can furnish two H^+ per molecule. (5.3)

Disaccharide: A carbohydrate whose molecules can be hydrolyzed to two monosaccharides. (23.6)

Dispersions: Mixtures of very small particles of immiscible substances that do not readily separate into different phases. Often used when describing emulsions. (13.8)

Dispersion Forces: Another term for London forces. (12.2)

Disproportionation: A redox reaction in which a portion of a substance is oxidized at the expense of the rest, which is reduced.

Dissociation: The separation of preexisting ions when an ionic compound dissolves or melts. (5.2)

Dissymmetric: Lacking or deficient in symmetry. In a dissymmetric molecule the effects of the individual bond dipoles do not cancel, causing the molecule as a whole to be polar. (10.3)

Distorted Tetrahedron: A description of a molecule in which the central atom is surrounded by five electron pairs, one of which is a lone pair of electrons. The central atom is bonded to four other atoms. The structure is also said to have a seesaw shape. (10.2)

DNA: Deoxyribonucleic acid; a nucleic acid that hydrolyzes to deoxyribose, phosphate ion, adenine, thymine, guanine, and cytosine, and that is the carrier of genes. (23.7)

DNA Double Helix: Two oppositely running strands of DNA held in a helical configuration by inter strand hydrogen bonds. (23.7)

Donor Atom: The atom on a ligand that makes an electron pair available in the formation of a complex. (18.4, 22.1)

Doped: A semiconductor material such as Si or Ge that has small amounts of electron rich (e.g., P) or electron deficient (e.g., B) atoms added. (10.9)

Double Bond: (a) A covalent bond formed by sharing two pairs of electrons. (9.5) (b) A covalent bond consisting of one sigma bond and one pi bond. (10.6)

Double Replacement Reaction (Metathesis Reaction): A reaction of two salts in which cations and anions exchange partners

$$(\text{e.g., } AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3).\ (5.5)$$

Downs Cell: An electrolytic cell for the industrial production of sodium. (20.9)

Ductility: A metal's ability to be drawn (or stretched) into wire. (3.3)

Dynamic Equilibrium: A condition in which two opposing processes are occurring at equal rates. (5.3, 14.1)

E

ΔE: See *Internal Energy Change.*

Effective Collision: A collision between molecules that is capable of leading to a net chemical change. (14.5)

Effective Nuclear Charge: The net positive charge an outer electron experiences as a result of the partial screening of the full nuclear charge by core electrons. (8.10)

Effusion: The movement of a gas through a very tiny opening into a region of lower pressure. (11.6)

Effusion, Law of (Graham's Law): The rates of effusion of gases are inversely proportional to the square roots of their densities when compared at identical pressures and temperatures.

$$\text{Effusion rate} \propto \frac{1}{\sqrt{d}} \quad (\text{constant } P \text{ and } T)$$

where d is the gas density. (11.6)

Einstein Equation: $\Delta E = m_0c^2$ where ΔE is the energy obtained when a quantity of rest mass, Δm_0, is destroyed, or the energy lost when this quantity of mass is created. (21.1)

Electric Dipole: Two poles of electric charge separated by a distance. (9.7)

Electrochemical Change: A chemical change that is caused by or that produces electricity. (20 Introduction)

Electrochemistry: The study of electrochemical changes. (20 Introduction)

Electrolysis: The production of a chemical change by the passage of electricity through a solution that contains ions or through a molten ionic compound. (20.7)

Electrolysis Cell: An apparatus for electrolysis. (20.7)

Electrolyte: A compound that conducts electricity either in solution or in the molten state. (5.2)

Electrolytic Cell: See *Electrolysis Cell.*

Electrolytic Conduction: The transport of electrical charge by ions. (20.1)

Electromagnetic Radiation: (See *Electromagnetic Wave*)

Electromagnetic Spectrum: The distribution of frequencies of electromagneticradiation among various types of such radiation—microwave, infrared, visible, ultraviolet, X rays, and gamma rays. (8.1)

Electromagnetic Wave (Electromagnetic Radiation): The successive series of oscillations in the strengths of electrical and magnetic fields associated with light, microwaves, gamma rays, ultraviolet rays, infrared rays, and the like. (8.1)

Electron (e^- or $_{-1}^{0}e$): (a) A subatomic particle with a charge of 1– and mass of 0.0005486 u (9.109383×10^{-28} g) that occurs outside an atomic nucleus. The particle that moves when an electric current flows. (3.1) (b) A beta particle. (21.3)

Electron Affinity (EA): The energy change (usually expressed in kJ mol^{-1}) that occurs when an electron adds to an isolated gaseous atom or ion. (8.10)

Electron Capture: The capture by a nucleus of an orbital electron and that changes a proton into a neutron in the nucleus. (21.3)

Electron Cloud: Because of its wave properties, an electron's influence spreads out like a cloud around the nucleus. (8.9)

Electron Configuration: The distribution of electrons in an atom's orbitals. (8.7)

Electron Density: The concentration of the electron's charge within a given volume. (8.9)

Electron Domain: A region around an atom where one or more electron pairs are concentrated and which influences the shape of a molecule. (10.2)

Electron Domain Model: See *Valence Shell Electron Pair Repulsion Model.*

Electron Pair Bond: A covalent bond. (9.5)

Electron Spin: The spinning of an electron about its axis that is believed to occur because the electron behaves as a tiny magnet. (8.6)

Electron Volt (eV): The energy an electron receives when it is accelerated under the influence of 1 V and equal to 1.6×10^{-19} J. (29.3)

Electronegativity: The relative ability of an atom to attract electron density toward itself when joined to another atom by a covalent bond. (9.7)

Electronic Structure: The distribution of electrons in an atom's orbitals. (8.7)

Electroplating: Depositing a thin metallic coating on an object by electrolysis. (20.9)

Element: A substance in which all of the atoms have the same atomic number.

A substance that cannot be broken down by chemical reactions into anything that is both stable and simpler. (1.3, 3.1)

Elementary Process: One of the individual steps in the mechanism of a reaction. (14.8)

Elimination Reaction: The loss of a small molecule from a larger molecule as in the elimination of water from an alcohol. (23.3)

Emission Spectrum: See *Atomic Spectrum*.

Empirical Formula: A chemical formula that uses the smallest whole-number subscripts to give the proportions by atoms of the different elements present. (4.3)

Emulsion: A mixture of small globules of one immiscible liquid in another. (13.8)

Enantiomers: Stereoisomers whose molecular structures are related as an object to its mirror image but that cannot be superimposed. (22.4)

End Point: The moment in a titration when the indicator changes color and the titration is ended. (5.8, 17.9)

Endergonic: Descriptive of a change accompanied by an increase in free energy. (19.4)

Endothermic: Descriptive of a change in which a system's internal energy increases. (7.4)

Energy: Something that matter possesses by virtue of an ability to do work. (7.1)

Energy Band: Closely spaced energy levels in materials that can be described as a band of energy (10.9)

Energy Density: For a galvanic cell, the ratio of the energy available to the volume of the cell. (20.6)

Energy Level: A particular energy an electron can have in an atom or a molecule. (8.3)

English System: Old system of weights and measures that includes such units as pounds, ounces, gallons and miles. (2.2)

Enthalpy (*H*): The heat content of a system. (7.6, 19.1)

Enthalpy Change (Δ*H*): The difference in enthalpy between the initial state and the final state for some change. (7.6, 19.1)

Enthalpy Diagram: A graphical depiction of enthalpy changes following different paths from reactants to products. (7.8)

Enthalpy of Solution: See *Heat of Solution*.

Entropy (*S*): A thermodynamic quantity related to the number of equivalent ways the energy of a system can be distributed. The greater this number, the more probable is the state and the higher is the entropy. (19.3)

Entropy Change (Δ*S*): The difference in entropy between the initial state and the final state for some change. (19.4)

Enzyme: A catalyst in a living system and that consists of a protein. (23.6)

Equation of State of an Ideal Gas: See *Gas Law, Ideal.*

Equatorial Bond: A covalent bond located in the plane perpendicular to the long axis of a trigonal bipyramidal molecule. (10.1)

Equilibrium: See *Dynamic Equilibrium*.

Equilibrium Constant, *K*: The value that the mass action expression has when the system is at equilibrium. (15.2)

Equilibrium Law: The mathematical equation for a particular equilibrium system that sets the mass action expression equal to the equilibrium constant. (15.2)

Equilibrium Vapor Pressure of a Liquid: The pressure exerted by a vapor in equilibrium with its liquid state. (12.5)

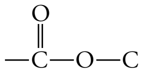
Equilibrium Vapor Pressure of a Solid: The pressure exerted by a vapor in equilibrium with its solid state. (12.5)

Equivalence: A relationship between two quantities expressed in different units. (2.4)

Equivalence Point: The moment in a titration when the number of equivalents of the reactant added from a buret equals the number of equivalents of another reactant in the receiving flask. (17.9)

Error in a Measurement: The difference between a measurement and the "true" value we are trying to measure. (2.3)

Ester: An organic compound whose molecules have the ester group. (23.3)



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-C$$

ester group

Ether: An organic compound in whose molecules two hydrocarbon groups are joined to an oxygen. (23.3)

Ethyl Group: Alkyl group derived from ethane, $–CH_2CH_3$ (23.2)

Evaporation: Change of state from a liquid to a vapor. (12.3)

Exact Number: A number obtained by a direct count or that results by a definition; and that is considered to have an infinite number of significant figures. (2.3)

Excess Reactant: The reactant left over once the limiting reactant is used up. (4.5)

Excited State: A term describing an atom or molecule where all of the electrons are not in their lowest possible energy levels. (8.2)

Exergonic: Descriptive of a change accompanied by a decrease in free energy. (19.4)

Exothermic: Descriptive of a change in which energy leaves a system and enters the surroundings. (7.4)

Expansion Work: See *Pressure–Volume Work*.

Exponential Notation: See *Scientific Notation*.

Extensive Property: A property of an object that is described by a physical quantity whose magnitude is proportional to the size or amount of the object (e.g., mass or volume). (2.1)

F

Face-Centered Cubic (fcc) Unit Cell: A unit cell having identical atoms, molecules, or ions at the corners of a cube and also in the center of each face of the cube. (12.11)

Factor-Label Method: See *Dimensional Analysis*

Fahrenheit Scale: A temperature scale on which water freezes at 32 °F and boils at 212 °F (at 1 atm) and between which points there are 180 degree divisions called Fahrenheit degrees. (2.2)

Family of Elements: See *Group*.

Faraday ($\mathscr{F}$): One mole of electrons; 9.65×10^4 coulombs. (20.4)

Faraday Constant ($\mathscr{F}$): 9.65×10^4 coulombs/mol e^-. (20.4)

Fatty Acid: One of several long-chain carboxylic acids produced by the hydrolysis (digestion) of a lipid. (23.6)

Film Dosimeter: A device used by people working with radioactive isotopes that records doses of atomic radiation by the darkening of photographic film. (21.6)

First Law of Thermodynamics: A formal statement of the law of conservation of energy. $\Delta E = q + w$. (7.5, 19.1)

First-Order Reaction: A reaction with a rate law in which rate $= k[A]^1$, where A is a reactant. (14.4)

Fissile Isotope: An isotope capable of undergoing fission following neutron capture. (21.8)

Fission: The breaking apart of atomic nuclei into smaller nuclei accompanied by the release of energy, and the source of energy in nuclear reactors. (21.2, 21.8)

Force: Anything that can cause an object to change its motion or direction.

Formal Charge: The apparent charge on an atom in a molecule or polyatomic ion as calculated by a set of rules. (9.8)

Formation Constant (K_{form}): The equilibrium constant for an equilibrium involving the formation of a complex ion. Also called the stability constant. (18.4)

Formula: See *Chemical Formula*.

Formula Mass: The sum of the atomic masses (in u) of all of the atoms represented in a chemical formula. Often used with units of g mol^{-1} to represent masses of ionic substances. (4.1) See also *Molar Mass*.

Formula Unit: A particle that has the composition given by the chemical formula. (3.4)

Forward Reaction: In a chemical equation, the reaction as read from left to right. (5.3, 15.1)

Fossil Fuels: Coal, oil, and natural gas.

Free Element: An element that is not combined with another element in a compound. (1.5)

Free Energy: See *Gibbs Free Energy* or *Standard Free Energy Change*

Free Energy Diagram: A plot of the changes in free energy for a multicomponent system versus the composition. (19.8)

Free Radical: An atom, molecule, or ion that has one or more unpaired electrons. (Chemistry Outside the Classroom 14.1, 21.6)

Freezing Point Depression: A colligative property of a liquid solution by which the freezing point of the solution is lower than that of the pure solvent. (13.7)

Frequency (ν): The number of cycles per second of electromagnetic radiation. (8.1)

Frequency Factor: The proportionality constant, A, in the Arrhenius equation. (14.7)

Fuel: Commonly one component of a combustion reaction; specifically the reducing agent. (7.9)

Fuel Cell: An electrochemical cell in which electricity is generated from the redox reactions of common fuels. (20.6)

Fullerene: An allotrope of carbon made of an extended joining together of five- and six-membered rings of carbon atoms. (10.10)

Functional Group: The group of atoms of an organic molecule that enters into a characteristic set of reactions that are independent of the rest of the molecule. (9.6)

Fusion: (a) Melting. (12.4) (b) The formation of atomic nuclei by the joining together of the nuclei of lighter atoms. (21.2, 21.8)

G

G: See *Gibbs Free Energy.*

ΔG: See *Gibbs Free Energy Change.*

$\Delta G°$: See *Standard Free Energy Change.*

$\Delta G_f°$: See *Standard Free Energy of Formation.*

Galvanic Cell: An electrochemical cell in which a spontaneous redox reaction produces electricity. (20.1)

Gamma Radiation: Electromagnetic radiation with wavelengths in the range of 1 Å or less (the shortest wavelengths of the spectrum). (20.3)

Gas: One of the states of matter. A gas consists of rapidly moving widely spaced atomic or molecular sized particles. (2.1)

Gas Constant, Universal (R): $R = 0.0821$ liter atm mol^{-1} K^{-1} or $R = 8.314$ J mol^{-1} K^{-1} (11.5)

Gas Law, Combined: For a given mass of gas, the product of its pressure and volume divided by its Kelvin temperature is a constant. (11.3)

$$PV/T = \text{a constant}$$

Gas Law, Ideal: $PV = nRT$. (11.5)

Gay-Lussac's Law: See *Pressure–Temperature Law.*

Geiger Counter: A device that detects beta and gamma radiation. (21.6)

Genetic Code: The correlation of codons with amino acids. (23.7)

Geometric Isomer: One of a set of isomers that differ only in geometry. (22.4, 23.2)

Geometric Isomerism: The existence of isomers whose molecules have identical atomic organizations but different geometries; cis-trans isomers. (22.4, 23.2)

Gibbs Free Energy (G): A thermodynamic quantity that relates enthalpy (H), entropy (S), and temperature (T) by the equation: (19.4)

$$G = H - TS$$

Gibbs Free Energy Change (ΔG): The difference given by: (19.4)

$$\Delta G = \Delta H - T\Delta S$$

Glass: Any amorphous solid. (12.11)

Global climate change: A term used to describe the overall effect of man-made and natural substances in the atmosphere that may cause heating or cooling of the Earth. (11.9)

Glycogen: A polysaccharide that animals use to store glucose units for energy. (23.6)

Graham's Law: See *Effusion, Law of.*

Gram (g): 0.001 kg. (2.2)

Graphene: A sheet of graphite, one atom thick. (10.10)

Graphite: The most stable allotrope of carbon, consisting of layers of joined six-membered rings of carbon atoms. (10.10)

Gray (Gy): The SI unit of radiation absorbed dose. (21.6)

$$1\ \text{Gy} = 1\ \text{J kg}^{-1}$$

Greenhouse Effect: The retention of solar energy made possible by the ability of the greenhouse gases (e.g., CO_2, CH_4, H_2O, and the chlorofluorocarbons) to absorb outgoing radiation and reradiate some of it back to earth. (11.9)

Ground State: The lowest energy state of an atom or molecule. (8.3)

Group: A vertical column of elements in the periodic table. (3.2)

H

ΔH: See *Enthalpy Change.*

ΔH_{atom}: See *Atomization Energy.*

ΔH_c: See *Heat of Combustion.*

$\Delta H°$: See *Standard Heat of Reaction.*

$\Delta H_f°$: See *Standard Heat of Formation.*

ΔH_{fusion}: See *Molar Heat of Fusion.*

ΔH_{soln}: See *Heat of Solution.*

$\Delta H_{\text{sublimation}}$: See *Molar Heat of Sublimation.*

$\Delta H_{\text{vaporization}}$: See *Molar Heat of Vaporization.*

Half-Cell: That part of a galvanic cell in which either oxidation or reduction takes place. (20.1)

Half-Life ($t_{1/2}$): The time required for a reactant concentration or the mass of a radionuclide to be reduced by half. (14.4)

Half-Reaction: A hypothetical reaction that constitutes exclusively either the oxidation or the reduction half of a redox reaction and all species taking part in the change are given together with enough electrons to give the correct electrical balance. (6.2)

Hall–Héroult Process: A method for manufacturing aluminum by the electrolysis of aluminum oxide in molten cryolite. (20.8)

Halogen Family: Group 7A in the periodic table—fluorine, chlorine, bromine, iodine, and astatine. (3.2)

Hard Water: Water with dissolved Mg^{2+}, Ca^{2+}, Fe^{2+}, or Fe^{3+} ions at a concentration high enough (above 25 mg L^{-1}) to interfere with the use of soap. (Chemistry Outside the Classroom 5.2)

Heat: Energy that flows from a hot object to a cold object as a result of their difference in temperature. (7.1)

Heat Capacity: The quantity of heat needed to raise the temperature of an object by 1 °C. (7.3)

Heat of Combustion (ΔH_c): The heat evolved in the combustion of a substance. (7.6)

Heat of Formation, Standard: See *Standard Heat of Formation.*

Heat of Reaction: The heat exchanged between a system and its surroundings when a chemical change occurs in the system. (7.5)

Heat of Reaction at Constant Pressure (q_p): The heat of a reaction in an open system, ΔH. (7.5, 19.1)

Heat of Reaction at Constant Volume (q_v): The heat of a reaction in a sealed vessel, like a bomb calorimeter, ΔE. (7.6)

Heat of Reaction, Standard: See *Standard Heat of Reaction.*

Heat of Solution (ΔH_{soln}): The energy exchanged between the system and its surroundings when one mole of a solute dissolves in a solvent to make a dilute solution. (13.2)

Heating Curve: A graph showing how the temperature of a substance changes as heat is added to it at a constant rate as the substance undergoes changes in its physical state. (12.7)

Henderson–Hasselbalch Equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]_{\mathrm{initial}}}{[HA]_{\mathrm{initial}}} \quad \text{or}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]} \quad (16.5)$$

(17.7)

Henry's Law: See *Pressure–Solubility Law*.

Hertz (Hz): 1 cycle s^{-1}; the SI unit of frequency. (8.1)

Hess's Law: For any reaction that can be written in steps, the standard heat of reaction is the same as the sum of the standard heats of reaction for the steps. (7.8)

Hess's Law Equation: For the change,

$$aA + bB + \cdots \longrightarrow nN + mM + \cdots \quad (6.8)$$

$$\Delta H^\circ = \begin{pmatrix}\text{sum of } \Delta H_f^\circ \text{ of all} \\ \text{of the products}\end{pmatrix} - \begin{pmatrix}\text{sum of } \Delta H_f^\circ \text{ of all} \\ \text{of the reactants}\end{pmatrix}$$

(7.9)

Heterocyclic Rings: Molecular rings that include one or more multivalent atoms other than carbon. (23.1)

Heterogeneous Catalyst: A catalyst that is in a different phase than the reactants and onto whose surface the reactant molecules are adsorbed and where they react. (14.9)

Heterogeneous Equilibrium: An equilibrium involving more than one phase. (15.4)

Heterogeneous Mixture: A mixture that has two or more phases with different properties. (1.3)

Heterogeneous Reaction: A reaction in which not all of the chemical species are in the same phase. (14.1, 15.4)

Heteronuclear Molecule: A molecule in which not all atoms are of the same element. (10.7)

Hexagonal Closest Packing (hcp): Efficient packing of spheres with an A-B-A-B-. . . alternating stacking of layers of spheres. (12.11)

High-Spin Complex: A complex ion or coordination compound in which there is the maximum number of unpaired electrons. (22.5)

Hole: An electron deficient site in a semiconductor. A positive charge carrier. (20.6)

Homogeneous Catalyst: A catalyst that is in the same phase as the reactants. (14.9)

Homogeneous Equilibrium: An equilibrium system in which all components are in the same phase. (15.2)

Homogeneous Mixture: A mixture that has only one phase and that has uniform properties throughout; a solution. (1.3)

Homogeneous Reaction: A reaction in which all of the chemical species are in the same phase. (14.1, 15.2)

Homonuclear Diatomic Molecule: A diatomic molecule in which both atoms are of the same element. (10.7)

Hund's Rule: Electrons that occupy orbitals of equal energy are distributed with unpaired spins as much as possible among all such orbitals. (8.7)

Hybrid Atomic Orbitals: Orbitals formed by mixing two or more of the basic atomic orbitals of an atom and that make possible more effective overlaps with the orbitals of adjacent atoms than do ordinary atomic orbitals. (10.5)

Hydrate: A compound that contains molecules of water in a definite ratio to other components. (1.5)

Hydrated Ion: An ion surrounded by a cage of water molecules that are attracted by the charge on the ion. (5.2)

Hydration: The development in an aqueous solution of a cage of water molecules about ions or polar molecules of the solute. (13.1)

Hydration Energy: The enthalpy change associated with the hydration of gaseous ions or molecules as they dissolve in water. (13.2)

Hydride: (a) A binary compound of hydrogen. (3.6) (b) A compound containing the hydride ion (H^-).

Hydrocarbon: An organic compound whose molecules consist entirely of carbon and hydrogen atoms. (3.6, 23.2)

Hydrogen Bonding: An extra strong dipole–dipole attraction between a hydrogen bound covalently to nitrogen, oxygen, or fluorine and another nitrogen, oxygen, or fluorine atom. (12.2)

Hydrogen Electrode: The standard of comparison for reduction potentials and for which $E^\circ_{H^+}$ has a value of 0.00 V at 25 °C, when $P_{H_2} = 1$ atm and $[H^+] = 1\ M$ in the reversible half-cell reaction: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$. (20.2)

Hydrolysis: A reaction with water (16.6, 17.6)

Hydrometer: A device for measuring specific gravity. (20.6)

Hydronium Ion: H_3O^+. (5.3)

Hydrophilic: Miscible with water, literally, "water loving." (13.8, 23.6)

Hydrophilic Group: A polar molecular unit capable of having dipole–dipole attractions or hydrogen bonds with water molecules. (23.6)

Hydrophobic. Not miscible with water, literally, "afraid of water." (13.8, 23.6)

Hydrophobic Group: A nonpolar molecular unit with no affinity for water. (22.7)

Hypertonic Solution: A solution that has a higher osmotic pressure than cellular fluids. (13.7)

Hypothesis: A tentative explanation of the results of experiments. (1.2)

Hypotonic Solution: A solution that has a lower osmotic pressure than cellular fluids. (13.7)

Hypoxia: Condition of natural water where there is not dissolved oxygen to support aquatic life. (13.3)

I

Ideal Gas: A hypothetical gas that obeys the gas laws exactly. (11.3)

Ideal Gas Law: $PV = nRT$. (11.5)

Ideal Solution: A hypothetical solution that would obey the vapor pressure–concentration law (Raoult's law) exactly. (13.2)

Immiscible: Mutually insoluble. Usually used to describe liquids that are insoluble in each other. (13.1)

Incompressible: Incapable of losing volume under increasing pressure. (12.3)

Independent Variable: The experimental variable of a pair of variables whose value is first selected and from which the value of the dependent variable then results.

Indicator: A chemical put in a solution being titrated and whose change in color signals the end point. (5.8, 17.9)

Induced Dipole: A dipole created when the electron cloud of an atom or a molecule is distorted by a neighboring dipole or by an ion. (12.2)

Inert Gas: See *Noble Gases*

Initiation Step: The step in a chain reaction that produces reactive species that can start chain propagation steps. (Chemistry Outside the Classroom 14.1)

Inner Transition Elements: Members of the two long rows of elements below the main body of the periodic table—elements 58–71 and elements 90–103. (3.2)

Inorganic Compound: A compound made from any elements except those compounds of carbon classified as organic compounds. (3.5)

Instability Constant (K_{inst}): The reciprocal of the formation constant for an equilibrium in which a complex ion forms. (18.4)

Instantaneous Dipole: A momentary dipole in an atom, ion, or molecule caused by the erratic movement of electrons. (12.2)

Instantaneous Rate: The rate of reaction at any particular moment during a reaction. (14.2)

Integrated Rate Law: A rate law that relates concentration versus time. (14.4)

Intensive Property: A property whose physical magnitude is independent of the size of the sample, such as density or temperature. (2.1)

Intercalation: The insertion of small atoms or ions between layers in a crystal such as graphite. (20.6)

Interference Fringes: Pattern of light produced by waves that undergo diffraction. (8.4)

Intermolecular Forces (Intermolecular Attractions): Attractions *between* neighboring molecules. (12.2)

Internal Energy (*E*): The sum of all of the kinetic energies and potential energies of the particles within a system. (7.2, 19.1)

Internal Energy Change (ΔE): The difference in internal energy between the initial state and the final state for some change. (7.2)

International System of Units (SI): The successor to the metric system of measurements that retains most of the units of the metric system and their decimal relationships but employs new reference standards. (2.2)

Intramolecular Forces: Forces of attraction within molecules; chemical bonds. (11.2)

Inverse Square Law: The intensity of a radiation is inversely proportional to the square of the distance from its source. (21.6)

Ion: An electrically charged particle on the atomic or molecular scale of size. (3.4)

Ion–Dipole Attraction: The attraction between an ion and the charged end of a polar molecule. (12.2)

Ion–Electron Method: A method for balancing redox reactions that uses half-reactions. (6.2)

Ion–Induced Dipole Attraction: Attraction between an ion and a dipole induced in a neighboring molecule. (12.2)

Ion Pair: A more or less loosely associated pair of ions in a solution. (13.7)

Ion Product: The mass action expression for the solubility equilibrium involving the ions of a salt and equal to the product of the molar concentrations of the ions, each concentration raised to a power that equals the number of ions obtained from one formula unit of the salt. (18.1)

Ion Product Constant of Water (K_w): $K_w = [H^+][OH^-]$ (17.1)

Ionic Bond: The attractions between ions that hold them together in ionic compounds. (9.2)

Ionic Character: The extent to which a covalent bond has a dipole moment and is polarized. (9.7)

Ionic Compound: A compound consisting of positive and negative ions. (3.4)

Ionic Crystal: A crystal that has ions located at the lattice points. (12.13)

Ionic Equation: A chemical equation in which soluble strong electrolytes are written in dissociated or ionized form. (5.2)

Ionic Reaction: A chemical reaction in which ions are involved. (5.2)

Ionization Energy (IE): The energy needed to remove an electron from an isolated, gaseous atom, ion, or molecule (usually given in units of kJ mol^{-1}). (8.10)

Ionization Reaction: A reaction of chemical particles that produces ions. (5.3)

Ionizing Radiation: Any high-energy radiation—X rays, gamma rays, or radiations from radionuclides—that generates ions as it passes through matter. (22.6)

Isolated System: A system that cannot exchange matter or energy with its surroundings. (7.3)

Isomer: One of a set of compounds that have identical molecular formulas but different structures. (22.4)

Isomerism: The existence of sets of isomers. (9.6, 22.4)

Isopropyl Group: Alkyl group derived from propane, $—CH(CH_3)_2$ (23.2)

Isothermal: A system where the temperature remains unchanged. (19.1)

Isotonic Solution: A solution that has the same osmotic pressure as cellular fluids. (12.8)

Isotopes: Atoms of the same element with different atomic masses. Atoms of the same element with different numbers of neutrons in their nuclei. (3.1)

IUPAC Rules: The formal rules for naming substances as developed by the International Union of Pure and Applied Chemistry. (3.5, 23.2)

J

Joule (J): The SI unit of energy. (7.1)

$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$

$4.184\ \text{J} = 1\ \text{cal}$ (exactly)

K

K: See *Kelvin.*

K_a: See *Acid Ionization Constant.*

K_b: See *Base Ionization Constant.*

K_{form}: See *Formation Constant.*

K_{inst}: See *Instability Constant.*

K_{sp}: See *Solubility Product Constant.*

K_{spa}: See *Acid Solubility Product.*

K_w: See *Ion Product Constant of Water.*

K-Capture: See *Electron Capture.*

Kelvin (K): One degree on the Kelvin scale of temperature and identical in size to the Celsius degree. (2.2)

Kelvin Scale: The temperature scale on which water freezes at 273.15 K and boils at 373.15 K and that has 100 degree divisions called kelvins between these points. K = °C + 273.15. (2.2)

Ketone: An organic compound whose molecules have the carbonyl group ($C{=}O$) flanked by hydrocarbon groups. (9.6)

Kilocalorie (kcal): 1000 cal. (7.1)

Kilogram (kg): The base unit for mass in the SI and equal to the mass of a cylinder of platinum–iridium alloy kept by the International Bureau of Weights and Measures at Sevres, France. 1 kg = 1000 g. (2.2)

Kilojoule (kJ): 1000 J. (7.1)

Kinetic Energy (KE): Energy of motion. $\text{KE} = (1/2)mv^2$. (7.1)

Kinetic Molecular Theory: Molecules of a substance are in constant motion with a distribution of kinetic energies at a given temperature. The average kinetic energy of the molecules is proportional to the Kelvin temperature. (7.2)

Kinetic Molecular Theory of Gases: A set of postulates used to explain the gas laws. A gas consists of an extremely large number of very tiny, very hard particles in constant, random motion. They have negligible volume and, between collisions, experience no forces between themselves. (11.7)

L

Lanthanide Elements: Elements 58–71. (3.2)

Lattice: A symmetrical pattern of points arranged with constant repeat distances along lines oriented at constant angles. (12.11)

Lattice Energy: Energy released by the imaginary process in which isolated ions come together to form a crystal of an ionic compound. (9.2)

Law: A description of behavior (and not an *explanation* of behavior) based on the results of many experiments. (1.2)

Law of Combining Volumes: When gases react at the same temperature and pressure, their combining volumes are in ratios of simple whole numbers. (11.4)

Law of Conservation of Energy: The energy of the universe is constant; it can be neither created nor destroyed but only transferred and transformed. (7.1)

Law of Conservation of Mass: No detectable gain or loss in mass occurs in chemical reactions. Mass is conserved. (1.4)

Law of Conservation of Mass–Energy: The sum of all the mass in the universe and of all of the energy, expressed as an equivalent in mass (calculated by the Einstein equation), is a constant. (22.1)

Law of Definite Proportions: In a given chemical compound, the elements are always combined in the same proportion by mass. (1.4)

Law of Gas Effusion: See *Effusion, Law of.*

Law of Multiple Proportions: Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other are in a ratio of small whole numbers. (2.4)

Law of Partial Pressures: See *Partial Pressures, Dalton's Law of.*

Law of Radioactive Decay:

$$\text{Activity} = -\frac{\Delta N}{\Delta t} = kN,$$

where ΔN is the change in the number of radioactive nuclei during the time span Δt, and k is the decay constant. (21.6)

Le Châtelier's Principle: When a system that is in dynamic equilibrium is subjected to a disturbance that upsets the equilibrium, the system undergoes a change that counteracts the disturbance and, if possible, restores the equilibrium. (15.6)

Lead Storage Battery: A galvanic cell of about 2 V involving lead and lead(IV) oxide in sulfuric acid. (20.6)

Leclanché Cell: See *Zinc–Manganese Dioxide Cell.*

Lewis Acid: An electron-pair acceptor. (16.4)

Lewis Base: An electron-pair donor. (16.4)

Lewis Structure (Lewis Formula): A structural formula drawn with Lewis symbols and that uses dots and dashes to show the valence electrons and shared pairs of electrons. (9.5)

Lewis Symbol: The symbol of an element that includes dots to represent the valence electrons of an atom of the element. (9.4)

Ligand: A molecule or an anion that can bind to a metal ion to form a complex. (18.4, 22.1)

Light-Emitting Diode (LED): A semiconductor device where a small applied voltage will eject visible photons. (10.9)

Like Dissolves Like Rule: Strongly polar and ionic solutes tend to dissolve in polar solvents and nonpolar solutes tend to dissolve in nonpolar solvents. (13.1)

Limiting Reactant: The reactant that determines how much product can form when nonstoichiometric amounts of reactants are used. (4.5)

Line Spectrum: An atomic spectrum. So named because the light emitted by an atom and focused through a narrow slit yields a series of lines when projected on a screen. (8.1)

Linear Molecule: A molecule all of whose atoms lie on a straight line. (10.1, 10.2)

Lipid: Any substance found in plants or animals that can be dissolved in nonpolar solvents. (23.6)

Liquid: One of the states of matter. A liquid consists of tightly packed atomic or molecular sized particles that can move past each other. (2.1)

Liter (L): 1 dm^3. 1 L = 1000 mL = 1000 cm^3. (2.2)

Lithium Ion Cell: A cell in which lithium ions are transferred between the electrodes through an electrolyte, while electrons travel through the external circuit. (20.6)

Lithium–Manganese Dioxide Battery: A battery that uses metallic lithium as the anode and manganese dioxide as the cathode. (20.6)

Localized Bond: A covalent bond in which the bonding pair of electrons is localized between two nuclei.

London Forces (Dispersion Forces): Weak attractive forces caused by instantaneous dipole–induced dipole attractions. (12.2)

Lone Pair: A pair of electrons in the valence shell of an atom that is not shared with another atom. An unshared pair of electrons. (10.2)

Low-Spin Complex: A coordination compound or a complex ion with electrons paired as much as possible in the lower energy set of *d* orbitals. (22.5)

M

Macromolecule: A molecule whose molecular mass is very large. (23.5)

Macroscopic: A scale that includes masses in the range of 1 to 1000 g or the equivalent. Also considered the laboratory scale. (1.2)

Magic Numbers: The numbers 2, 8, 20, 28, 50, 82, and 126, numbers whose significance in nuclear science is that a nuclide in which the number of protons or neutrons equals a magic number has nuclei that are relatively more stable than those of other nuclides nearby in the band of stability. (21.4)

Magnetic Quantum Number (m_ℓ): A quantum number that can have values from zero to $N - 1$. (8.5)

Main Group Elements: Elements in any of the A groups in the periodic table. (3.2)

Main Reaction: The desired reaction between the reactants as opposed to competing reactions that give by-products. (4.6)

Malleability: A metal's ability to be hammered or rolled into thin sheets. (3.3)

Manometer: A device for measuring the pressure within a closed system. The two types—*closed end* and *open end*—differ according to whether the operating fluid (e.g., mercury) is exposed at one end to the atmosphere. (11.2)

Mass: A measure of the amount of matter that there is in a given sample. (1.3)

Mass Action Expression: A fraction in which the numerator is the product of the molar concentrations of the products, each raised to a power equal to its coefficient in the equilibrium equation, and the denominator is the product of the molar concentrations of the reactants, each also raised to the power that equals its coefficient in the equation. (For gaseous reactions, partial pressures can be used in place of molar concentrations.) (15.2)

Mass Defect: For a given isotope, it is the mass that changed into energy as the nucleons gathered to form the nucleus, this energy being released from the system. (21.2)

Mass Fraction: The ratio of the mass of one component of a mixture to the total mass of that same mixture. (13.5)

Mass Number: The numerical sum of the protons and neutrons in an atom of a given isotope. (3.1)

Matter: Anything that has mass and occupies space. (1.3)

Mean: The sum of *N* numerical values divided by *N*; the average. (2.3)

Measurement: A numerical observation. (2.2)

Mechanism of a Reaction: The series of individual steps (called elementary processes) in a chemical reaction that gives the net, overall change. (14.8)

Melting Point: The temperature at which a substance melts; the temperature at which a solid is in equilibrium with its liquid state. (12.4)

Meniscus: The interface between a liquid and a gas.

Metal: An element or an alloy that is a good conductor of electricity, that has a shiny surface, and that is malleable and ductile; an element that normally forms positive ions and has an oxide that is basic. (3.3)

Metallic Conduction: Conduction of electrical charge by the movement of electrons. (20.1)

Metallic Crystal: A solid having positive ions at the lattice positions that are attracted to a "sea of electrons" that extends throughout the entire crystal. (12.13)

Metalloids: Elements with properties that lie between those of metals and nonmetals, and that are found in the periodic table around the diagonal line running from boron (B) to astatine (At). (3.3)

Metathesis Reaction: See *Double Replacement Reaction.*

Meter (m): The SI base unit for length. (2.2)

Methyl Group: Alkyl group derived from methane, —CH_3

Metric Units: A decimal system of units for physical quantities taken over by the SI. (2.2) See also *International System of Units.*

Micelle: A structure formed from molecules that have a hydrophobic and hydrophilic end. The result is a circular or spherical structure with the molecules forming a rudimentary membrane. (13.8)

Millibar: 1 mb = 10^{-3} bar. (11.2)

Milliliter (mL): 0.001 L. 1000 mL = 1 L. (2.2)

Millimeter (mm): 0.001 m. 1000 mm = 1 m. (2.2)

Millimeter of Mercury (mm Hg): A unit of measurement that is proportional to pressure; equal to 1/760 atm. 760 mm Hg = 1 atm. 1 mm Hg = 1 torr. (11.2)

Miscible: Mutually soluble. (13.1)

Mixture: Any matter consisting of two or more substances physically combined in no particular proportion by mass. (1.3)

MO Theory: See *Molecular Orbital Theory.*

Model, Theoretical: A picture or a mental construction derived from a set of ideas and assumptions that are imagined to be true because they can be used to explain certain observations and measurements (e.g., the model of an ideal gas). (1.2)

Mol L^{-1} s^{-1}: See *Rate of Reaction*

Molal Boiling Point Elevation Constant (K_b): The number of degrees (°C) per unit of molal concentration that a boiling point of a solution is higher than that of the pure solvent. (13.7)

Molal Concentration (m): The number of moles of solute in 1000 g of solvent. (13.5)

Molal Freezing Point Depression Constant (K_f): The number of degrees (°C) per unit of molal concentration that a freezing point of a solution is lower than that of the pure solvent. (13.7)

Molality: The molal concentration. (13.5)

Molar Concentration (M): The number of moles of solute per liter of solution. The molarity of a solution. (5.6)

Molar Enthalpy of Solution: See *Heat of Solution.*

Molar Heat Capacity: The heat that can raise the temperature of 1 mol of a substance by 1 °C; the heat capacity per mole. (7.3)

Molar Heat of Fusion, ΔH_{fusion}: The heat absorbed when 1 mol of a solid melts to give 1 mol of the liquid at constant temperature and pressure. (12.7)

Molar Heat of Sublimation, $\Delta H_{\text{sublimation}}$: The heat absorbed when 1 mol of a solid sublimes to give 1 mol of its vapor at constant temperature and pressure. (12.7)

Molar Heat of Vaporization, $\Delta H_{\text{vaporization}}$: The heat absorbed when 1 mol of a liquid changes to 1 mol of its vapor at constant-temperature and pressure. (12.7)

Molar Mass: The mass of one mole of a substance; the mass in grams equal to the sum of the atomic masses of the atoms in a substance, with units of g mol^{-1}. (4.1)

Molar Solubility: The number of moles of solute required to give 1 L of a saturated solution of the solute. (18.1)

Molar Volume, Standard: The volume of 1 mol of a gas at STP; 22.4 L mol^{-1}. (11.4)

Molarity: See *Molar Concentration.*

Mole (mol): The SI unit for amount of substance; the formula mass in grams of an element or compound; an amount of a chemical substance that contains 6.022×10^{23} formula units. (4.1)

Mole Fraction: The ratio of the number of moles of one component of a mixture to the total number of moles of all components. (11.6)

Mole Percent (mol%): The mole fraction of a component expressed as a percent; mole fraction × 100%. (11.6, 13.5)

Molecular Compound: A compound consisting of electrically neutral molecules. (2.6)

Molecular Crystal: A crystal that has molecules or individual atoms at the lattice points. (12.13)

Molecular Equation: A chemical equation that gives the full formulas of all of the reactants and products and that is used to plan an actual experiment. (5.2)

Molecular Formula: A chemical formula that gives the actual composition of one molecule. (3.6, 4.3)

Molecular Kinetic Energy: The energy associated with the motions of and within molecules as they fly about, spinning and vibrating. (7.2)

Molecular Mass: The sum of the atomic masses (in u) of all of the atoms represented in a molecular chemical substance; also called the *molecular weight.* May be used with units of g mol^{-1}. (4.1) See also *Molar Mass.*

Molecular Orbital (MO): An orbital that extends over two or more atomic nuclei. (10.7)

Molecular Orbital Theory (MO Theory): A theory about covalent bonds that views a molecule as a collection of positive nuclei surrounded by electrons distributed among a set of bonding, antibonding, and nonbonding orbitals of different energies. (10.4)

Molecular Weight: See *Molecular Mass.*

Molecule: A neutral particle composed of two or more atoms combined in a definite ratio of whole numbers. (1.5, 3.6)

Monatomic: A particle consisting of just one atom. (3.5)

Monoclinic Sulfur: An allotrope of sulfur. (10.10)

Monodentate Ligand: A ligand that can attach itself to a metal ion by only one atom. (22.1)

Monomer: A substance of relatively low formula mass that is used to make a polymer. (23.5)

Monoprotic Acid: An acid that can furnish one H^+ per molecule. (5.3)

Monosaccharide: A carbohydrate that cannot be hydrolyzed. (23.6)

N

n-type Semiconductor: A semiconductor that carries electrical charge by means of electron movement. (10.9)

Nanotechnology: The study and use of unique properties of matter that has dimensions measured in nanometers. (1.6)

Negative Charge: A type of electrical charge possessed by certain particles such as the electron. A negative charge is attracted by a positive charge and is repelled by another negative charge. (3.1)

Negative Charge Carrier: In a semiconductor, the electrons are considered to be negative charge carriers. (20.6)

Nernst Equation: An equation relating cell potential and concentration. (20.5)

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{n\mathcal{F}}\ln Q$$

Net Ionic Equation: A chemical equation that shows only the reacting ions and from which spectator ions have been omitted. It is balanced when both atoms and electrical charge balance. (5.2)

Network Solid: See *Covalent Crystal.*

Neutral Solution: A solution in which $[H^+] = [OH^-]$. (17.1)

Neutralization, Acid–Base: See *Acid–Base Neutralization.*

Neutron: A subatomic particle with a charge of zero, a mass of 1.0086649 u (1.674927×10^{-24} g) and that exists in all atomic nuclei except those of the hydrogen-1 isotope. (3.1)

Neutron Activation Analysis: A technique to analyze for trace impurities in a sample by studying the frequencies and intensities of the gamma radiations they emit after they have been rendered radioactive by neutron bombardment of the sample. (21.7)

Neutron Emission: A nuclear reaction in which a neutron is ejected. (21.3)

Nicad Battery: A nickel–cadmium cell. (20.6)

Nickel–Cadmium Storage Cell: A galvanic cell of about 1.4 V involving the reaction of cadmium with nickel(IV) oxide. (20.6)

Nitrogen Family: Group 5A in the periodic table—nitrogen, phosphorus, arsenic, antimony, and bismuth. (3.2)

Noble Gases: Group 8A in the periodic table—helium, neon, argon, krypton, xenon, and radon. (3.2)

Noble Metals: The group of transition metals, including gold, silver and platinum, that have relatively low chemical reactivity. (9.7)

Nodal Plane: A plane that can be drawn to separate opposing lobes of *p*, *d*, and *f* orbitals. (8.9)

Node: A place where the amplitude or intensity of a wave is zero. (8.4)

Nomenclature: The names of substances and the rules for devising names. (3.5)

Nonbonding Domain: A region in the valence shell of an atom that holds an unshared pair of electrons and that influences the shape of a molecule. (10.2)

Nonbonding Molecular Orbital: A molecular orbital that has no net effect on the stability of a molecule when populated with electrons and that is localized on one atom in the molecule. (10.7)

Nonelectrolyte: A compound that in its molten state or in solution cannot conduct electricity. (5.2)

Nonlinear Molecule: A molecule in which the atoms do not lie in a straight line. (10.2)

Nonmetal: A nonductile, nonmalleable, nonconducting element that tends to form negative ions (if it forms them at all) far more readily than positive ions and whose oxide is likely to show acidic properties. (3.3)

Nonmetal Hydrides: Usually binary compounds that contain hydrogen and a nonmetal. (3.6)

Nonmetallic Element: See *Nonmetals*

Nonoxidizing Acid: An acid in which the anion is a poorer oxidizing agent than the hydrogen ion (e.g., HCl, H_2SO_4, H_3PO_4). (6.3)

Nonpolar Covalent Bond: A covalent bond in which the electron pair(s) are shared equally by the two atoms. (9.7)

Nonpolar Molecule: A molecule that has no net dipole moment. (9.3)

Nonvolatile: Descriptive of a substance with a high boiling point, a low vapor pressure. and that does not evaporate. (12.6)

Normal Boiling Point: The temperature at which the vapor pressure of a liquid equals 1 atm. (12.6)

Nuclear Binding Energy: See *Binding Energy, Nuclear.*

Nuclear Chain Reaction: A self-sustaining nuclear reaction. (21.8)

Nuclear Equation: A description of a nuclear reaction that uses the special symbols of isotopes, that describes some kind of nuclear transformation or disintegration, and that is balanced when the sums of the atomic numbers on either side of the arrow are equal and the sums of the mass numbers are also equal. (21.3)

Nuclear Fission: See *Fission.*

Nuclear Fusion: See *Fusion.*

Nuclear Radiation: Alpha, beta, or gamma radiation emitted by radioactive nuclei. (21.3)

Nuclear Reaction: A change in the composition or energy of the nuclei of isotopes accompanied by one or more events such as the radiation of nuclear particles or electromagnetic energy, transmutation, fission, or fusion. (13.4, 20.3)

Nucleic Acids: Polymers in living cells that store and translate genetic information and whose molecules hydrolyze to give a sugar unit (ribose from ribonucleic acid, RNA, or deoxyribose from deoxyribonucleic acid, DNA), a phosphate, and a set of four of the five nitrogen-containing, heterocyclic bases (adenine, thymine, guanine, cytosine, and uracil). (23.7)

Nucleon: A proton or a neutron. (3.1, 21.2)

Nucleus: The hard, dense core of an atom that holds the atom's protons and neutrons. (3.1)

Nylon 6,6: A polymer of a six-carbon dicarboxylic acid and a six-carbon diamine. (23.5)

O

Observation: A statement that accurately describes something we see, hear, taste, feel, or smell. (1.2)

Octahedral Molecule: A molecule in which a central atom is surrounded by six atoms located at the vertices of an imaginary octahedron. (10.1)

Octahedron: An eight-sided figure that can be envisioned as two square pyramids sharing the common square base. (10.1)

Octet (of Electrons): Eight electrons in the valence shell of an atom. (9.3)

Octet Rule: An atom tends to gain or lose electrons until its outer shell has eight electrons. (9.3, 9.5)

Odd–Even Rule: When the numbers of protons and neutrons in an atomic nucleus are both even, the isotope is more likely to be stable than when both numbers are odd. (21.4)

Open System: A system that can exchange both matter and energy with its surroundings. (7.3)

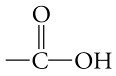
Open-End Manometer: See *Manometer.*

Optical Isomers: Stereoisomers other than geometric (cis–trans) isomers and that include substances that can rotate the plane of plane-polarized light. (22.4)

Orbital: An electron waveform with a particular energy and a unique set of values for the quantum numbers *n*, *ℓ*, and m_ℓ. (8.5)

Orbital Diagram: A diagram in which the electrons in an atom's orbitals are represented by arrows to indicate paired and unpaired spins. (8.7)

Order (of a Reaction): The sum of the exponents in the rate law is the *overall* order. Each exponent gives the order of the reaction with respect to a specific reactant. (14.3)

Organic Acid: An acid that contains the carboxyl group,  $-\overset{\displaystyle O}{\overset{\|}{C}}-OH$ (8.3, 9.6, 22.6)

Organic Chemistry: The study of the compounds of carbon that are not classified as inorganic. (3.6, 23.1)

Organic Compound: Any compound of carbon other than a carbonate, bicarbonate, cyanide, cyanate, carbide, or gaseous oxide. (3.5, 9.6)

Orthorhombic Sulfur: The most stable allotrope of sulfur, composed of S_8 rings. (10.10)

Osmosis: The passage of solvent molecules, but not those of solutes, through a semipermeable membrane; the limiting case of dialysis. (13.7)

Osmotic Membrane: A membrane that allows passage of solvent, but not solute particles. (13.7)

Osmotic Pressure: The back pressure that would have to be applied to prevent osmosis; one of the colligative properties. (13.7)

Outer Electrons: The electrons in the occupied shell with the largest principal quantum number. An atom's electrons in its valence shell. (8.8)

Outer Shell: The occupied shell in an atom having the highest principal quantum number (n). (8.8)

Overall Order of Reaction: The sum of the exponents on the concentration terms in a rate law. (14.3)

Overlap of Orbitals: A portion of two orbitals from different atoms that share the same space in a molecule. (10.4)

Oxidation: A change in which an oxidation number increases (becomes more positive). A loss of electrons. (6.1)

Oxidation Number: The charge that an atom in a molecule or ion would have if all of the electrons in its bonds belonged entirely to the more electronegative atoms; the oxidation state of an atom. (6.1)

Oxidation State: See *Oxidation Number*.

Oxidation–Reduction Reaction: A chemical reaction in which changes in oxidation numbers occur. (6.1)

Oxidizing Acid: An acid in which the anion is a stronger oxidizing agent than H^+ (e.g., $HClO_4$, HNO_3). (6.3)

Oxidizing Agent: The substance that causes oxidation and that is itself reduced. (6.1)

Oxoacid: An acid that contains oxygen besides hydrogen and another element (e.g., HNO_3, H_3PO_4, H_2SO_4). (5.4, 16.3)

Oxoanion: The anion of an oxoacid (e.g., ClO_4^-, SO_4^{2-}). (16.3)

Oxygen Family: Group 6A in the periodic table—oxygen, sulfur, selenium, tellurium, and polonium.

Ozone: A very reactive allotrope of oxygen with the formula O_3. (11.9)

Ozone Hole: The large decrease of stratospheric ozone at the Earth's poles at the end of winter each year; ascribed to the effect of chlorine compounds. (11.9)

P

p-n Junction: The surface where a p-type semiconductor and an n-type semiconductor meet. (10.9)

p-type Semiconductor: A semiconductor material with a deficit of electrons causing charge to be carried by positive charge carriers or "holes." (10.9)

Pairing Energy: The energy required to force two electrons to become paired and occupy the same orbital. (22.5)

Paramagnetism: The weak magnetism of a substance whose atoms, molecules, or ions have one or more unpaired electrons. (8.6)

Partial Charge: Charges at opposite ends of a dipole that are fractions of full 1+ or 1− charges. (9.7)

Partial Pressure: The pressure contributed by an individual gas to the total pressure of a gas mixture. (11.6)

Partial Pressure, Law of (Dalton's Law of Partial Pressures): The total pressure of a mixture of gases equals the sum of their partial pressures. (11.6)

Pascal (Pa): The SI unit of pressure equal to 1 newton m^{-2}; 1 atm = 101,325 Pa. (11.2)

Pauli Exclusion Principle: No two electrons in an atom can have the same values for all four of their quantum numbers. (8.6)

Peptide Bond: The amide linkage in molecules of polypeptides. (23.6)

Percentage Composition: A list of the percentages by weight of the elements in a compound. (4.2)

Percentage Concentration: A ratio of the amount of solute to the amount of solution expressed as a percent. (5.1)
Weight/weight: Grams of solute in 100 g of solution.
Weight/volume: Grams of solute in 100 mL of solution.
Volume/volume: Volumes of solute in 100 volumes of solution.

Percentage Ionization: An equation that quantifies the ionization of a substance in solution. (17.4)

Percentage ionization

$$= \frac{\text{amount of substance ionized}}{\text{initial amount of substance}} \times 100\%$$

Percentage by Mass (Percentage by Weight): (a) The number of grams of an element combined in 100 g of a compound. (4.2) (b) The number of grams of a substance in 100 g of a mixture or solution. (13.5)

Percentage Yield: The ratio (taken as a percent) of the mass of product obtained to the mass calculated from the reaction's stoichiometry. (4.6)

Period: A horizontal row of elements in the periodic table. (3.2)

Periodic Table: A table in which symbols for the elements are displayed in order of increasing atomic number and arranged so that elements with similar properties lie in the same column (group). (Inside front cover, 3.2)

pH: $-\log [H^+]$. (17.1)

Phase: A homogeneous region within a sample. (1.3)

Phase Diagram: A pressure–temperature graph on which are plotted the temperatures and the pressures at which equilibrium exists between the states of a substance. It defines regions of T and P in which the solid, liquid, and gaseous states of the substance can exist. (12.10)

Photoelectric Effect: The phenomenon whereby energetic photons can eject electrons from certain materials. (8.1)

Photon: A unit of energy in electromagnetic radiation equal to $h\nu$, where ν is the frequency of the radiation and h is Planck's constant. (8.1)

Photosynthesis: The use of solar energy by a plant to make high-energy molecules from carbon dioxide, water, and minerals. (8.1)

Physical Change: A change that is not accompanied by a change in chemical makeup. (1.3)

Physical Law: A relationship between two or more physical properties of a system, usually expressed as a mathematical equation, that describes how a change in one property affects the others.

Physical Property: A property that can be specified without reference to another substance and that can be measured without causing a chemical change. (2.1)

Physical State: The condition of aggregation of a substance's formula units, whether as a solid, a liquid, or a gas. (1.4)

Pi Bond (π Bond): A bond formed by the sideways overlap of a pair of p orbitals and that concentrates electron density into two separate regions that lie on opposite sides of a plane that contains an imaginary line joining the nuclei. (10.6)

pK_a: $-\log K_a$. (17.3)

pK_b: $-\log K_b$. (17.3)

pK_w: $-\log K_w$. (17.1)

Planar Triangular Molecule: A molecule in which a central atom holds three other atoms located at the corners of an equilateral triangle and that includes the central atom at its center. (10.1)

Plane-Polarized Light: Light in which all the oscillations occur in one plane. (22.4)

Planck's Constant (*h*): The ratio of the energy of a photon to its frequency; $6.6260755 \times 10^{-34}$ J Hz^{-1}. (8.1)

Plasma: An electrically neutral, very hot gaseous mixture of nuclei and unattached electrons. (21.8)

pOH: $-\log [OH^-]$. (17.1)

Polar Covalent Bond (Polar Bond): A covalent bond in which more than half of the bond's negative charge is concentrated around one of the two atoms. (9.7)

Polar Molecule: A molecule in which individual bond polarities do not cancel and in which, therefore, the centers of density of negative and positive charges do not coincide. (9.7)

Polarizability: A term that describes the ease with which the electron cloud of a molecule or ion is distorted. (12.2)

Polyatomic Ion: An ion composed of two or more atoms. (3.4)

Polydentate Ligand: A ligand that has two or more atoms that can become simultaneously attached to a metal ion. (22.1)

Polymer: A substance consisting of macromolecules that have repeating structural units. (23.5)

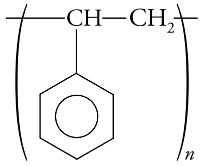
Polymerization: A chemical reaction that converts a monomer into a polymer. (23.5)

Polypeptide: A polymer of α-amino acids that makes up all or most of a protein. (23.6)

Polyprotic Acid: An acid that can furnish more than one H^+ per molecule. (5.3)

Polysaccharide: A carbohydrate whose molecules can be hydrolyzed to hundreds of monosaccharide molecules. (23.6)

Polystyrene: An addition polymer of styrene with the following structure.



polystyrene (23.5)

Position of Equilibrium: The relative amounts of the substances on both sides of the double arrows in the equation for an equilibrium. (5.3, 12.9, 15.5)

Positive Charge: A type of electrical charge possessed by certain particles such as the proton. A positive charge is attracted by a negative charge and is repelled by another positive charge. (3.1)

Positive Charge Carrier: In a semiconductor material doped with an electron deficient element, the holes carry the charge. (20.6)

Positron ($^{1}_{0}p$): A positively charged particle with the mass of an electron. (21.3)

Post-transition Metal: A metal that occurs in the periodic table immediately to the right of a row of transition elements. (3.4)

Potential: See *Volt.*

Potential Energy (PE): Stored energy. (7.1)

Potential Energy Diagram: A diagram indicating the conversion of kinetic energy to potential energy and back again as atoms or molecules collide and then recoil in a chemical reaction. (13.5)

Precipitate: A solid that separates from a solution usually as the result of a chemical reaction. (5.1)

Precipitation Reaction: A reaction in which a precipitate forms. (5.1, 5.5)

Precision: How reproducible measurements are; the fineness of a measurement as indicated by the number of significant figures reported in the physical quantity. (2.3)

Pre-exponential Factor: A number or variable that precedes the exponential part of a number. (14.7)

Pressure: Force per unit area. (7.5, 11.2)

Pressure–Concentration Law: See *Vapor Pressure–Concentration Law.*

Pressure–Solubility Law (Henry's Law): The concentration of a gas dissolved in a liquid at any given temperature is directly proportional to the partial pressure of the gas above the solution. $C_{\text{gas}} = k_{\text{H}}P_{\text{gas}}$. (13.4)

Pressure–Temperature Law (Gay-Lussac's Law): The pressure of a given mass of gas is directly proportional to its Kelvin temperature if the volume is kept constant. $P \propto T$. (11.3)

Pressure–Volume Law (Boyle's Law): The volume of a given mass of a gas is inversely proportional to its pressure if the temperature is kept constant. $V \propto 1/P$. (11.3)

Pressure–Volume Work (*P–V* Work): The energy transferred as work when a system expands or contracts against the pressure exerted by the surroundings. At constant pressure, $w = -P\,\Delta V$. (7.5)

Primary Cell: A galvanic cell (battery) not designed to be recharged; it is discarded after its energy is depleted. (20.6)

Primitive Cubic Unit Cell: See *Simple Cubic Unit Cell.*

Principal Quantum Number (*n*): The quantum number that defines the principal energy levels and that can have values of 1, 2, 3, . . . , ∞. (8.5)

Products: The substances produced by a chemical reaction and whose formulas follow the arrows in chemical equations. (1.6, 15.1)

Propagation Step: A step in a chain reaction for which one product must serve in a succeeding propagation step as a reactant and for which another (final) product accumulates with each repetition of the step. (Chemistry Outside the Classroom 14.1)

Property: A characteristic of matter. (2.1)

Propyl Group: Alkyl group derived from propane, $\text{—}CH_2CH_2CH_3$.

Protein: A macromolecular substance found in cells that consists wholly or mostly of one or more polypeptides that often are combined with an organic molecule or a metal ion. (23.6)

Proton ($^{1}_{1}p$ or $^{1}_{1}H^+$): (a) A subatomic particle, with a charge of 1+ and a mass of 1.0072765 u ($1.6726217 \times 10^{-24}$ g) and that is found in atomic nuclei. (3.1) (b) The name often used for the hydrogen ion and symbolized as H^+.

Proton Acceptor: A Brønsted base. (16.1)

Proton Donor: A Brønsted acid. (16.1)

Pure Substance: An element or a compound. (1.3)

Q

Qualitative Analysis: The use of experimental procedures to determine what elements are present in a substance. (5.8)

Qualitative Observation: Observations that do not involve numerical information. (2.2)

Quanta: Packets of electromagnetic radiation now commonly called photons. (8.1)

Quantitative Analysis: The use of experimental procedures to determine the percentage composition of a compound or the percentage of a component of a mixture. (5.8)

Quantitative Observation: An observation involving a measurement and numerical information. (2.2)

Quantized: Descriptive of a discrete, definite amount as of *quantized energy.* (8.3)

Quantum: The energy of one photon. (8.1)

Quantum Mechanics: See *Wave Mechanics.*

Quantum Number: A number related to the energy, shape, or orientation of an orbital, or to the spin of an electron. (8.3)

Quantum Theory: The physics of objects that exhibit wave/particle duality. (8 Introduction)

R

***R*:** See *Gas Constant, Universal.*

Rad (rd): A unit of radiation-absorbed dose and equal to 10^{-5} J g^{-1} or 10^{-2} Gy. (21.6)

Radioactive Decay: The change of a nucleus into another nucleus (or into a more stable form of the same nucleus) by the loss of a small particle or a gamma ray photon. (21.3)

Radioactive Disintegration Series: A sequence of nuclear reactions beginning with a very long-lived radionuclide and ending with a stable isotope of lower atomic number. (21.3)

Radioactivity: The emission of one or more kinds of radiation from an isotope with unstable nuclei. (21.3)

Radiological Dating: A technique for measuring the age of a geologic formation or an ancient artifact by determining the ratio of the concentrations of two isotopes, one radioactive and the other a stable decay product. (13.4, 21.7)

Radionuclide: A radioactive isotope. (21.3)

Raoult's Law: See *Vapor Pressure–Concentration Law*.

Rare Earth Metals: The lanthanides.

Rate: A ratio in which a unit of time appears in the denominator, for example, 40 miles hr^{-1} or 3.0 mol L^{-1} s^{-1}. (14.2)

Rate Constant (*k*): The proportionality constant in the rate law; the rate of reaction when all reactant concentrations are 1 *M*. (14.3)

Rate Law: An equation that relates the rate of a reaction to the molar concentrations of the reactants raised to powers. (14.3)

Rate of Reaction: How quickly the reactants disappear and the products form and usually expressed in units of mol L^{-1} s^{-1}. (14.1, 14.2)

Rate-Determining Step (Rate-Limiting Step): The slowest step in a reaction mechanism. (14.8)

Reactant, Limiting: See *Limiting Reactant*.

Reactants: The substances brought together to react and whose formulas appear before the arrow in a chemical equation. (1.6, 15.1)

Reaction Coordinate: The horizontal axis of a potential energy diagram of a reaction. (14.6)

Reaction Mechanism: A sequence of elementary processes that sum to the overall reaction and possess one process that can derive the experimental rate law. (14.8)

Reaction Quotient (*Q*): The numerical value of the mass action expression. (15.2) See *Mass Action Expression*.

Reactivity: A description of the tendency for a substance to undergo reaction. For a metal, it is the tendency to undergo oxidation. (9.7)

Red Phosphorus: A relatively unreactive allotrope of phosphorus. (10.10)

Redox Reaction: An oxidation–reduction reaction. (6.1)

Reducing Agent: A substance that causes reduction and is itself oxidized. (6.1)

Reduction: A change in which an oxidation number decrease (becomes less positive and more negative). A gain of electrons. (6.1)

Reduction Potential: A measure of the tendency of a given half-reaction to occur as a reduction. (20.2)

Rem: A dose in rads multiplied by a factor that takes into account the variations that different radiations have in their damage-causing abilities in tissue. (20.6)

Replication: In nucleic acid chemistry, the reproductive duplication of DNA double helices prior to cell division. (23.7)

Representative Element: An element in one of the A groups in the periodic table. (3.2)

Resonance: A concept in which the actual structure of a molecule or polyatomic ion is represented as a composite or average of two or more Lewis structures, which are called the resonance or contributing structures (and none of which has real existence). (9.9)

Resonance Energy: The difference in energy between a substance and its principal resonance (contributing) structure. (9.9)

Resonance Hybrid: The actual structure of a molecule or polyatomic ion taken as a composite or average of the resonance or contributing structures. (9.9)

Resonance Structure: A Lewis structure that contributes to the hybrid structure in resonance-stabilized systems; a contributing structure. (9.9)

Reverse Osmosis: The procedure where a pressure, exceeding the osmotic pressure, is applied to an osmotic membrane to force pure solvent from a mixture. (13.7)

Reverse Reaction: In a chemical equation, the reaction as read from right to left. (5.3, 15.1)

Reversible Reaction: A reaction capable of proceeding in either the forward or reverse direction. (13.5, 14.7, 19.7)

Ring, Carbon: A closed-chain sequence of carbon atoms. (23.1)

RNA: Ribonucleic acid; a nucleic acid that gives ribose, phosphate ion, adenine, uracil, guanine, and cytosine when hydrolyzed. It occurs in several varieties. (23.7)

Rock Salt Structure: The face-centered cubic structure observed for sodium chloride, which is also possessed by crystals of many other compounds. (12.11)

Root Mean Square Speed (rms Speed): The square root of the average of the speeds-squared of the molecules in a substance. (11.7)

Rydberg Equation: An equation used to calculate the wavelengths of all the spectral lines of hydrogen. (8.2)

S

Salt: An ionic compound in which the anion is not OH^- or O^{2-} and the cation is not H^+. (5.2, 5.3)

Salt Bridge: A tube that contains an electrolyte that connects the two half-cells of a galvanic cell. (20.1)

Saponification: The reaction of an organic ester with a strong base to give an alcohol and the salt of the organic acid. (23.3)

Saturated Organic Compound: A compound whose molecules have only single bonds. (23.2)

Saturated Solution: A solution that holds as much solute as it can at a given temperature. A solution in which there is an equilibrium between the dissolved and the undissolved states of the solute. (5.1, 18.1)

Scanning Tunneling Microscope (STM): An instrument that enables the imaging of individual atoms on the surface of an electrically conducting specimen. (1.4)

Scientific Law: See *Law*.

Scientific Method: The observation, explanation, and testing of an explanation by additional experiments. (1.2)

Scientific Notation: The representation of a quantity as a decimal number between 1 and 10 multiplied by 10 raised to a power (e.g., 6.02×10^{23}). (2.3)

Scintillation Counter: A device for measuring nuclear radiation that contains a sensor composed of a substance called a *phosphor* that emits a tiny flash of light when struck by a particle of ionizing radiation. These flashes can be magnified electronically and automatically counted. (21.6)

Second Law of Thermodynamics: Whenever a spontaneous event takes place, it is accompanied by an increase in the entropy of the universe. (19.4)

Second-Order Reaction: A reaction with a rate law of the type: rate $= k[A]^2$ or rate $= k[A][B]$, where A and B are reactants. (14.4)

Secondary Cell: A galvanic cell (battery) designed for repeated use; it is able to be recharged. (20.6)

Secondary Quantum Number (ℓ): The quantum number whose values can be 0, 1, 2, … , $(n - 1)$, where n is the principal quantum number. (8.5)

Seesaw Shaped Molecule: A description given to a molecule in which the central atom has five electron pairs in its valence shell, one of which is a lone pair and the others are used in bonds to other atoms. (10.2) See also *Distorted Tetrahedron*.

Selective Precipitation: A technique that uses differences in the solubilities of specific salts to separate ions from each other. (18.3)

Semiconductor: A substance that conducts electricity weakly. (3.3)

Shell: All of the orbitals associated with a given value of n (the principal quantum number). (8.5)

SI (International System of Units): The modified metric system adopted in 1960 by the General Conference on Weights and Measures. (2.2)

Side Reaction: A reaction that occurs simultaneously with another reaction (the main reaction) in the same mixture to produce by-products.

Sievert (Sv): The SI unit for dose equivalent. The dose equivalent H is calculated from D (the dose in grays), Q (a measure of the effectiveness of the radiation at causing harm), and N (a variable that accounts for other modifying factors). $H = DQN$. (21.6)

Sigma Bond (σ Bond): A bond formed by the head-to-head overlap of two atomic orbitals and in which electron density becomes concentrated along and around the imaginary line joining the two nuclei. (10.6)

Significant Figures (Significant Digits): The digits in a physical measurement that are known to be certain plus the first digit that contains uncertainty. (2.3)

Simple Cubic Unit Cell: A cubic unit cell that has atoms only at the corners of the cell. (12.11)

Simplest Formula: See *Empirical Formula.*

Single Bond: A covalent bond in which a single pair of electrons is shared. (9.5)

Single Replacement Reaction: A reaction in which one element replaces another in a compound; usually a redox reaction. (6.4)

Skeletal Structure: A diagram of the arrangement of atoms in a molecule, which is the first step in constructing the Lewis structure. (9.8)

Skeleton Equation: An unbalanced equation showing only the formulas of reactants and products. (6.2)

Solar Battery: A battery that is charged by electrical current from photovoltaic cells. (10.9)

Solar Cell: A semiconductor device that produces electrical current and voltage in the presence of sunlight. (10.9)

Sol-Gel Process: A method for producing sol gels, very porous materials. (16.6)

Solid: One of the states of matter. A solid consists of tightly packed atomic or molecular sized particles held rigidly in place. (2.1)

Solubility: The ratio of the quantity of solute to the quantity of solvent in a saturated solution and that is usually expressed in units of (g solute)/(100 g solvent) at a specified temperature. (5.1)

Solubility Product Constant (K_{sp}): The equilibrium constant for the solubility of a salt and that, for a saturated solution, is equal to the product of the molar concentrations of the ions, each raised to a power equal to the number of its ions in one formula unit of the salt. (18.1) See also *Acid Solubility Product.*

Solubility Rules: A set of rules describing salts that are soluble and those that are insoluble. They enable the prediction of the formation of a precipitate in a metathesis reaction. (5.5)

Solute: Something dissolved in a solvent to make a solution. (5.1)

Solution: A homogeneous mixture in which all particles are of the size of atoms, small molecules, or small ions. (1.3, 5.1)

Solvation: The development of a cagelike network of a solution's solvent molecules about a molecule or ion of the solute. (13.1)

Solvation Energy: The enthalpy of the interaction of gaseous molecules or ions of solute with solvent molecules during the formation of a solution. (13.2)

Solvent: A medium, usually a liquid, into which something (a solute) is dissolved to make a solution. (5.1)

Space Filling Model: A method of depicting molecules by the shape and volume that the molecule actually occupies. (1.5)

***sp* Hybrid Orbital:** A hybrid orbital formed by mixing one *s* and one *p* atomic orbital. The angle between a pair of *sp* hybrid orbitals is 180°. (10.5)

sp^2 Hybrid Orbital: A hybrid orbital formed by mixing one *s* and two *p* atomic orbitals. sp^2 hybrids are planar triangular with the angle between two sp^2 hybrid orbitals being 120°. (10.5)

sp^3 Hybrid Orbital: A hybrid orbital formed by mixing one *s* and three *p* atomic orbitals. sp^3 hybrids point to the corners of a tetrahedron; the angle between two sp^3 hybrid orbitals is 109.5°. (10.5)

sp^3d Hybrid Orbital: A hybrid orbital formed by mixing one *s*, three *p*, and one *d* atomic orbital. sp^3d hybrids point to the corners of a trigonal bipyramid. (10.5)

sp^3d^2 Hybrid Orbital: A hybrid orbital formed by mixing one *s*, three *p*, and two *d* atomic orbitals. sp^3d^2 hybrids point to the corners of an octahedron. (10.5)

Specific Gravity: A dimensionless property of matter. Its value is determined by dividing the density by the density of water under the same conditions. (2.5)

Specific Heat (Specific Heat Capacity): The quantity of heat that will raise the temperature of 1 g of a substance by 1 °C, usually in units of cal g^{-1} $°C^{-1}$ or J g^{-1} $°C^{-1}$. (7.3)

Spectator Ion: An ion whose formula appears in an ionic equation identically on both sides of the arrow, that does not participate in the reaction, and that is excluded from the net ionic equation. (5.2)

Spectrochemical Series: A listing of ligands in order of their ability to produce a large crystal field splitting. (22.5)

Speed of Light (c): The speed at which light travels in a vacuum; 3.00×108 m s^{-1}. (7.1)

Spin Quantum Number (m_s): The quantum number associated with the spin of a subatomic particle and for the electron can have a value of $+\frac{1}{2}$ or $-\frac{1}{2}$. (8.6)

Spontaneous Change: A change that occurs by itself without outside assistance. (19.2)

Square Planar Molecule: A molecule with a central atom having four bonds that point to the corners of a square. (10.2)

Square Pyramid: A pyramid with four triangular sides and a square base. (10.2)

Stability Constant: See *Formation Constant.*

Stabilization Energy: See *Resonance Energy.*

Standard Atmosphere: See *Atmosphere, Standard*

Standard Cell Notation: A way of describing the anode and cathode half-cells in a galvanic cell. The anode half-cell is specified on the left, with the electrode material of the anode given first and a vertical bar representing the phase boundary between the electrode and the solution. Double bars represent the salt bridge between the half-cells. The cathode halfcell is specified on the right, with the material of the cathode given last. Once again, a single vertical bar represents the phase boundary between the solution and the electrode. (20.1)

Standard Cell Potential ($E°_{cell}$): The potential of a galvanic cell at 25 °C and when all ionic concentrations are exactly 1 *M* and the partial pressures of all gases are 1 atm. (20.2)

Standard Conditions of Temperature and Pressure (STP): Standard reference conditions for gases. 273 K (0 °C) and 1 atm (760 torr). (11.4)

Standard Electrode Potential: The electrode potential measured versus the standard hydrogen electrode at standard state conditions. (20.2)

Standard Enthalpy Change ($\Delta H°$): See *Standard Heat of Reaction.*

Standard Enthalpy of Formation ($\Delta H°_f$): See *Standard Heat of Formation.*

Standard Entropy ($S°$): The entropy of 1 mol of a substance at 25 °C and 1 atm. (19.5)

Standard Entropy Change ($\Delta S°$): The entropy change of a reaction when determined with reactants and products at 25 °C and 1 atm and on the scale of the mole quantities given by the coefficients of the balanced equation. (19.5)

Standard Entropy of Formation (ΔS_f°): The value of ΔS° for the formation of one mole of a substance from its elements in their standard states. (19.5)

Standard Free Energy Change (ΔG°): $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. (19.6)

Standard Free Energy of Formation (ΔG_f°): The value of ΔG° for the formation of *one* mole of a compound from its elements in their standard states. (19.6)

Standard Heat of Combustion: The enthalpy change for the combustion of one mole of a compound under standard conditions. (7.9)

Standard Heat of Formation (ΔH_f°): The amount of heat absorbed or evolved when one mole of the compound is formed from its elements in their standard states. (7.9)

Standard Heat of Reaction (ΔH°): The enthalpy change of a reaction when determined with reactants and products at 25 °C and 1 atm and on the scale of the mole quantities given by the coefficients of the balanced equation. (7.7)

Standard Hydrogen Electrode: See *Hydrogen Electrode*.

Standard Molar Volume: See *Molar Volume, Standard*.

Standard Reduction Potential, E°: The reduction potential of a half-reaction at 25 °C when all ion concentrations are 1 *M* and the partial pressures of all gases are 1 atm. Also called standard electrode potential. (20.2)

Standard Solution: Any solution whose concentration is accurately known. (5.8)

Standard State: The condition in which a substance is in its most stable form at 25 °C and 1 atm. (7.7, 7.9, 20.2)

Standing Wave: A wave whose peaks and nodes do not change position. (8.4)

Starch: A polymer of glucose used by plants to store energy. (23.6)

State: The set of specific values of the physical properties of a system—its composition, physical form, concentration, temperature, pressure, and volume. (7.2)

State Function: A quantity whose value depends only on the initial and final states of the system and not on the path taken by the system to get from the initial to the final state. (*P, V, T, H, S*, and *G* are all state functions.) (7.2)

State of Matter: A physical state of a substance: solid, liquid, or gas. (2.1) See also *Standard State*.

Steady State: A system where material or energy enter and exit at the same rate producing no observable changes in pressure, volume, temperature or amount of material. (11.9)

Step-Growth Polymer: See *Condensation Polymer*

Stereoisomerism: The existence of isomers whose structures differ only in spatial orientations (e.g., geometric isomers and optical isomers). (22.4)

Stock System: A system of nomenclature that uses Roman numerals to specify oxidation states. (3.5)

Stoichiometry: A description of the relative quantities by moles of the reactants and products in a reaction as given by the coefficients in the balanced equation. (4.1)

Stopcock: A valve on a buret that is used to control the flow of titrant. (5.8)

Stored Energy: See *Potential Energy*.

STP: See *Standard Conditions of Temperature and Pressure*.

Straight-Chain Compound: An organic compound in whose molecules the carbon atoms are joined in one continuous open-chain sequence. (23.1)

Strong Acid: An acid that is essentially 100% ionized in water. A good proton donor. An acid with a large value of K_a. (5.3)

Strong Base: Any powerful proton acceptor. A base with a large value of K_b. A metal hydroxide that dissociates essentially 100% in water. (5.3)

Strong Electrolyte: Any substance that ionizes or dissociates in water to essentially 100%. (5.2, 5.3)

Structural Formula (Lewis Structure): A chemical formula that shows how the atoms of a molecule or polyatomic ion are arranged, to which other atoms they are bonded, and the kinds of bonds (single, double, or triple). (9.5)

Subatomic Particles: Electrons, protons, neutrons, and atomic nuclei. (3.1)

Sublimation: The conversion of a solid directly into a gas without passing through the liquid state. (12.3)

Subscript: In a chemical formula, a number after a chemical symbol, written below the line, and indicating the number of the preceding atoms in the formula (e.g., CH_4). Subscripts are also used to differentiate many variables such as the acid ionization constant (K_a) and the base ionization constant (K_b). (1.5)

Subshell: All of the orbitals of a given shell that have the same value of their secondary quantum number, ℓ. (8.5)

Substance: See *Pure Substance*.

Substitution Reaction: The replacement of an atom or group on a molecule by another atom or group. (23.2, 23.3)

Superconductor: A material in a state in which it offers no resistance to the flow of electricity.

Supercooled Liquid: A liquid at a temperature below its freezing point. An amorphous solid. (12.11)

Supercritical Fluid: A substance at a temperature above its critical temperature. (12.10)

Superheated Liquid: The condition of a substance in its liquid state above its boiling point. (12.7)

Superheating: The process where a substance is heated to a temperature above its normal boiling point. (12.7)

Superimposability: A test of structural chirality in which a model of one structure and a model of its mirror image are compared to see if the two could be made to blend perfectly, with every part of one coinciding simultaneously with the parts of the other. (22.4)

Supersaturated Solution: A solution that contains more solute than it would hold if the solution were saturated. Supersaturated solutions are unstable and tend to produce precipitates. (5.1)

Surface Tension: A measure of the amount of energy needed to expand the surface area of a liquid. (12.3)

Surfactant: A substance that lowers the surface tension of a liquid and promotes wetting. (12.3)

Surroundings: That part of the universe other than the system being studied and separated from the system by a real or an imaginary boundary. (7.3)

Suspension: A heterogeneous mixture that will eventually separate into its component parts under the influence of gravity. (13.8)

Symmetric: An object is symmetric if it looks the same when rotated, reflected in a mirror, or reflected through a point. (10.3)

System: That part of the universe under study and separated from the surroundings by a real or an imaginary boundary. (7.3, 7.7)

T

$t_{1/2}$: See *Half-Life*.

T-Shaped Molecule: A molecule having five electron domains in its valence shell, two of which contain lone pairs. The other three are used in bonds to other atoms. The molecule has the shape of the letter T, with the central atom located at the intersection of the two crossing lines. (10.2)

Tarnishing: See *Corrosion*.

Temperature: A measure of the hotness or coldness of something. A property related to the average kinetic energy of the atoms and molecules in a sample. A property that determines the direction of heat flow—from high temperature to low temperature. (2.2, 7.1)

Temperature–Volume Law (Charles' Law): The volume of a given mass of a gas is directly proportional to its Kelvin temperature if the pressure is kept constant. $V \propto T$. (11.3)

Termination Step: A step in a chain reaction in which a reactive species needed for a chain propagation step disappears without helping to generate more of this species. (Chemistry Outside the Classroom 14.1)

Tetrahedral Molecule: A molecule with a central atom bonded to four other atoms located at the corners of an imaginary tetrahedron. (10.1)

Tetrahedron: A four-sided figure with four triangular faces and shaped like a pyramid. (10.1)

Theoretical Model: See *Model, Theoretical.*

Theoretical Yield: See *Yield, Theoretical*

Theory: A tested explanation of the results of many experiments. (1.2)

Thermal Decomposition: The decomposition of a substance caused by heating it. (21.3)

Thermal Energy: The molecular kinetic energy possessed by molecules as a result of the temperature of the sample. Energy that is transferred as heat. (7.1)

Thermal Equilibrium: A condition reached when two or more substances in contact with each other come to the same temperature. (7.2)

Thermal Property: A physical property, like heat capacity or heat of fusion, that concerns a substance's ability to absorb heat without changing chemically.

Thermochemical Equation: A balanced chemical equation accompanied by the value of $\Delta H°$ that corresponds to the mole quantities specified by the coefficients. (7.7)

Thermochemistry: The study of the energy changes of chemical reactions. (7 Introduction)

Thermodynamic Equilibrium Constant (K): The equilibrium constant that is calculated from $\Delta G°$ (the standard free energy change) for a reaction at T K by the equation, $\Delta G° = RT \ln K$. (19.9)

Thermodynamically Reversible: A process that occurs by an infinite number of steps during which the driving force for the change is just barely greater than the force that resists the change. (19.7)

Thermodynamics (Chemical Thermodynamics): The study of the role of energy in chemical change and in determining the behavior of materials. (7 Introduction, 19.1)

Third Law of Thermodynamics: For a pure crystalline substance at 0 K, $S = 0$. (19.5)

Titrant: The solution added from a buret during a titration. (5.8)

Titration: An analytical procedure in which a solution of unknown concentration is combined slowly and carefully with a standard solution until a color change of some indicator or some other signal shows that equivalent quantities have reacted. Either solution can be the titrant in a buret with the other solution being in a receiving flask. (5.8)

Titration Curve: For an acid–base titration, a graph of pH versus the volume of titrant added. (17.9)

Torr: A unit of pressure equal to 1/760 atm. 1 mm Hg. (11.2)

Tracer Analysis: The use of small amounts of a radioisotope to follow (trace) the course of a chemical or biological change. (21.7)

Trans Isomer: A stereoisomer whose uniqueness lies in having two groups that project on opposite sides of a reference plane. (22.4)

Transcription: The synthesis of mRNA at the direction of DNA. (23.7)

Transition Elements: The elements located between Groups 2A and 3A in the periodic table. (3.2)

Transition Metals: The transition elements. (3.2)

Transition State: The structure and energy of the substances in an elementary process of a reaction mechanism when the species involved have acquired the minimum amount of potential energy and geometric configuration needed for a successful reaction. (14.6)

Transition State Theory: A theory about the formation and breakup of activated complexes. (14.6)

Translation: The synthesis of a polypeptide at the direction of a molecule of mRNA. (23.7)

Transmutation: The conversion of one isotope into another. (21.5)

Transuranium Elements: Elements 93 and higher. (21.5)

Traveling Wave: A wave whose peaks and nodes move. (8.4)

Triacylglycerol: An ester of glycerol and three fatty acids. (23.6)

Trigonal Bipyramid: A six-sided figure made of two three-sided pyramids that share a common face. (10.1)

Trigonal Bipyramidal Molecule: A molecule with a central atom holding five other atoms that are located at the corners of a trigonal bipyramid. (10.1, 10.2)

Trigonal Pyramidal Molecule: A molecule that consists of an atom, situated at the top of a three-sided pyramid, that is bonded to three other atoms located at the corners of the base of the pyramid. (10.2)

Triple Bond: A covalent bond comprised of one sigma bond and two pi bonds. Three pairs of electrons are shared between two atoms. (10.6)

Triple Point: The temperature and pressure at which the liquid, solid, and vapor states of a substance can coexist in equilibrium. (12.10)

Triprotic Acid: An acid that can furnish three H^+ ions per molecule. (5.3)

Tyndall Effect: Colloidal dispersions scatter light while true solutions do not scatter light. This light scattering is known as the Tyndall effect. (13.8)

U

u: See *Atomic Mass Unit.*

Ultraviolet Catastrophe: The term given to the fact that classical physics predicts large amounts of ultraviolet radiation should be emitted from heated materials. In fact, very little ultraviolet radiation is produced. (7 Introduction)

Uncertainty: The amount by which a measured quantity deviates from the true or actual value. (2.3)

Uncertainty Principle: There is a limit to our ability to measure a particle's speed and position simultaneously. (8.9)

Unit Cell: The smallest portion of a crystal that can be repeated over and over in all directions to give the crystal lattice. (12.11)

Unit of Measurement: A reference quantity, such as the meter or kilogram, in terms of which the sizes of measurements can be expressed. (2.2)

Universal Gas Constant (R): See *Gas Constant, Universal.*

Universe: The system and surroundings taken together. (7.3)

Unsaturated Compound: A compound whose molecules have one or more double or triple bonds. (23.2)

Unsaturated Solution: Any solution with a concentration less than that of a saturated solution of the same solute and solvent. (5.1)

V

V-Shaped Molecule: See *Bent Molecule.*

Vacuum: An enclosed space containing no matter whatsoever. A *partial vacuum* is an enclosed space containing a gas at a very low pressure.

Valence Band: Very closely spaced energy levels of valence electrons, particularly in metals is called the valence band. (10.9)

Valence Bond Theory (VB Theory): A theory of covalent bonding that views a bond as being formed by the sharing of one pair of electrons between two overlapping atomic or hybrid orbitals. (10.4)

Valence Electrons: The electrons of an atom in its valence shell that participate in the formation of chemical bonds. (8.8)

Valence Shell: The electron shell with the highest principal quantum number, n, that is occupied by electrons. (8.8)

Valence Shell Electron Pair Repulsion Model (VSEPR Model): The bonding and nonbonding (lone pair) electron domains in the valence shell of an atom seek an arrangement that leads to minimum repulsions and thereby determine the geometry of a molecule. (10.2)

Van der Waals' Constants: Empirical constants that make the van der Waals' equation conform to the gas law behavior of a real gas. (11.8)

Van der Waals' Equation: An equation of state for a real gas that corrects V and P for the excluded volume and the effects of intermolecular attractions. (11.8)

Van der Waals' Forces: Attractive forces including dipole–dipole, ion–dipole, and induced dipole forces. (12.2)

Van't Hoff Factor (i): The ratio of the observed freezing point depression to the value calculated on the assumption that the solute dissolves as un-ionized molecules. (13.7)

Vapor Pressure: The pressure exerted by the vapor above a liquid (usually referring to the *equilibrium* vapor pressure when the vapor and liquid are in equilibrium with each other). (11.6, 12.5)

Vapor Pressure–Concentration Law (Raoult's Law): The vapor pressure of one component above a mixture of molecular compounds equals the product of its vapor pressure when pure and its mole fraction. (13.7)

Viscosity: A liquid's resistance to flow. (12.3)

Visible Spectrum: That region of the electromagnetic spectrum whose frequencies can be detected by the human eye. (8.1)

Volatile: Descriptive of a liquid that has a low boiling point, a high vapor pressure at room temperature, and therefore evaporates easily. (12.5, 13.7)

Volt (V): The SI unit of electric potential or emf in joules per coulomb. (20.2)

$$1\ \text{V} = 1\ \text{J C}^{-1}$$

Voltaic Cell: See *Galvanic Cell.*

Volumetric Flask: A piece of glassware calibrated to hold an exact volume of liquid. Volumetric flasks come in a variety of sizes. (5.6)

VSEPR Model: See *Valence Shell Electron Pair Repulsion Model.*

W

Wave: An oscillation that moves outward from a disturbance. (8.1)

Wave Function (ψ): A mathematical function that describes the intensity of an electron wave at a specified location in an atom. The square of the wave function at a particular location specifies the probability of finding an electron there. (8.4)

Wave Mechanics (Quantum Mechanics): A theory of atomic structure based on the wave properties of matter. (8 Introduction)

Wave/Particle Duality: A particle such as the electron behaves like a particle in some experiments and like a wave in others. (8 Introduction)

Wavelength (λ): The distance between crests in the wavelike oscillations of electromagnetic radiations. (8.1)

Weak Acid: An acid with a low percentage ionization in solution; a poor proton donor; an acid with a low value of K_a. (5.3)

Weak Base: A base with a low percentage ionization in solution; a poor proton acceptor; a base with a low value of K_b. (5.3)

Weak Electrolyte: A substance that has a low percentage ionization or dissociation in solution. (5.3)

Weighing: The operation of measuring the mass of something using a balance. (1.5)

Weight: The force with which something is attracted to the earth by gravity. (1.3)

Weight Percent: See *Percentage by Mass.*

Wetting: The spreading of a liquid across a solid surface. (12.3)

White Phosphorus: A very reactive allotrope of phosphorus consisting of tetrahedral P_4 molecules. (10.10)

Work (w): The energy expended in moving an opposing force through some particular distance. Work has units of *force* × *distance*. (6.1, 6.5, 18.1)

X

X Ray: A stream of very high-energy photons emitted by substances when they are bombarded by high-energy beams of electrons or are emitted by radionuclides that have undergone K-electron capture. (21.3)

Xerogel: An extremely low density material that, among other things, can serve as a very low weight insulating material. (16.6)

Y

Yield, Actual: The amount of a product obtained in a laboratory experiment. (4.6)

Yield, Percentage: The ratio, given as a percent, of the quantity of product actually obtained in a reaction to the theoretical yield. (4.6)

Yield, Theoretical: The amount of a product calculated by the stoichiometry of the reaction. (4.6)

Z

Zero-Order Reaction: A reaction that occurs at a constant rate regardless of the concentration of the reactant. (14.4)

Zinc–Manganese Dioxide Cell (Leclanché Cell): A galvanic cell of about 1.5 V involving zinc and manganese dioxide under mildly acidic conditions. (20.6)

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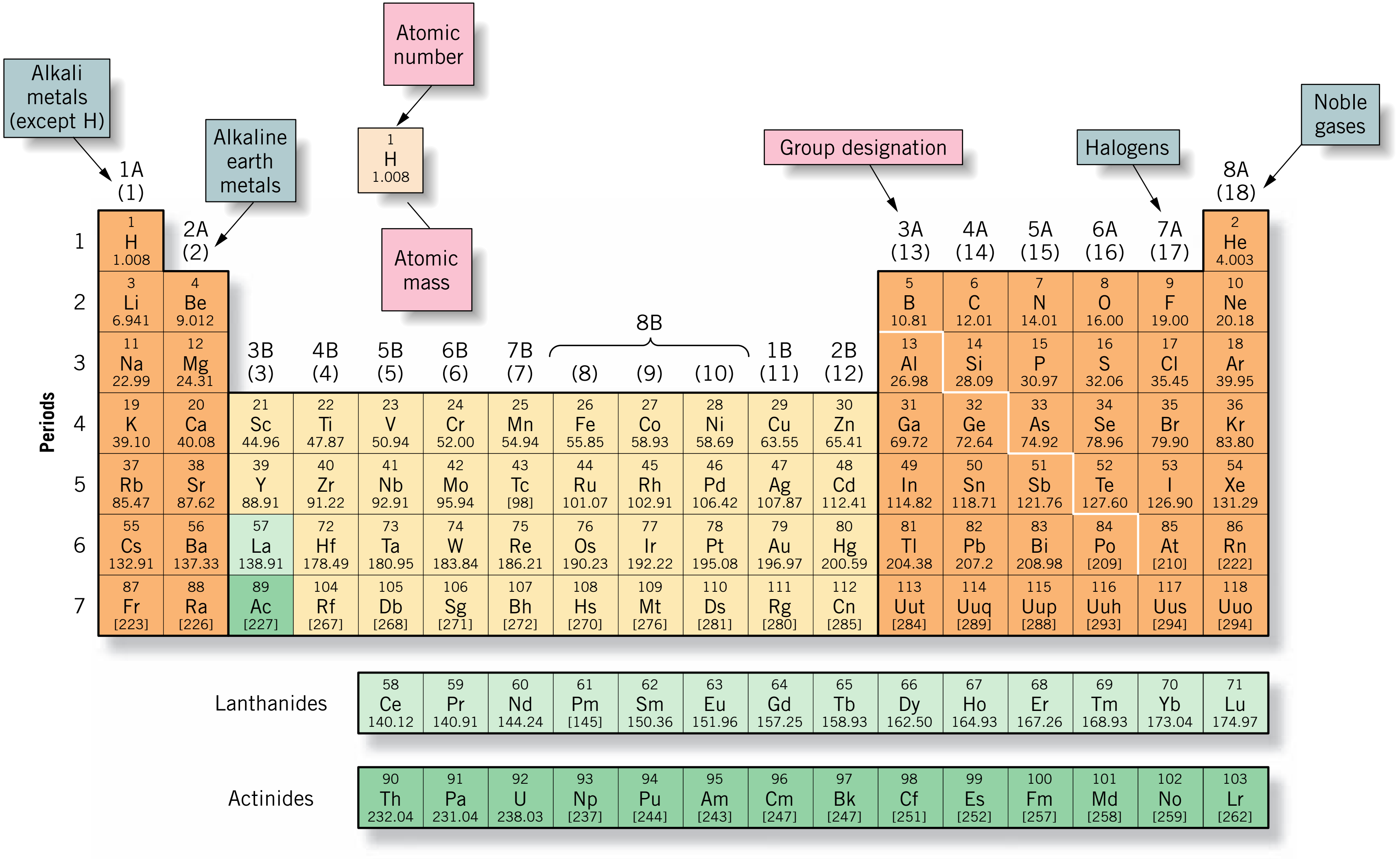
Periodic Table of the Elements


Alkali metals (except H)
Alkaline earth metals
Atomic number
1
H
1.008
Atomic mass
Group designation
Halogens
Noble gases
8B

Periods	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	(9)	(10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [267]	105 Db [268]	106 Sg [271]	107 Bh [272]	108 Hs [270]	109 Mt [276]	110 Ds [281]	111 Rg [280]	112 Cn [285]	113 Uut [284]	114 Uuq [289]	115 Uup [288]	116 Uuh [293]	117 Uus [294]	118 Uuo [294]

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

ATOMIC MASSES OF THE ELEMENTS

This table is based on the 2007 table at *Pure Appl. Chem.*, **81**, 2131–2156 (2009) with changes to the values for lutetium, molybdenum, nickel, ytterbium and zinc from the 2005 table. Mass number of the longest-lived isotope of hassium from *Phys. Rev. Lett.*, **97** 242501 (2006). For the name of element 112 see *Pure Appl. Chem.* 2010, **82**, 753–755. http://www.chem.qmul.ac.uk/iupac/AtWt/. The number in parentheses following the atomic mass is the estimated uncertainty in the last digit.

At No	Symbol	Name	Atomic Mass	Notes
89	Ac	Actinium	[227]	5
13	Al	Aluminium	26.9815386(8)	
95	Am	Americium	[243]	5
51	Sb	Antimony	121.760(1)	1
18	Ar	Argon	39.948(1)	1, 2
33	As	Arsenic	74.92160(2)	
85	At	Astatine	[210]	5
56	Ba	Barium	137.327(7)	
97	Bk	Berkelium	[247]	5
4	Be	Beryllium	9.012182(3)	
83	Bi	Bismuth	208.98040(1)	
107	Bh	Bohrium	[272]	5
5	B	Boron	10.811(7)	1, 2, 3
35	Br	Bromine	79.904(1)	
48	Cd	Cadmium	112.411(8)	1
55	Cs	Cesium	132.9054519(2)	
20	Ca	Calcium	40.078(4)	1
98	Cf	Californium	[251]	5
6	C	Carbon	12.0107(8)	1, 2
58	Ce	Cerium	140.116(1)	1
17	Cl	Chlorine	35.453(2)	3
24	Cr	Chromium	51.9961(6)	
27	Co	Cobalt	58.933195(5)	
112	Cn	Copernicium	[285]	5
29	Cu	Copper	63.546(3)	2
96	Cm	Curium	[247]	5
110	Ds	Darmstadtium	[281]	5
105	Db	Dubnium	[268]	5
66	Dy	Dysprosium	162.500(1)	1
99	Es	Einsteinium	[252]	5
68	Er	Erbium	167.259(3)	1
63	Eu	Europium	151.964(1)	1
100	Fm	Fermium	[257]	5
9	F	Fluorine	18.9984032(5)	
87	Fr	Francium	[223]	5
64	Gd	Gadolinium	157.25(3)	1
31	Ga	Gallium	69.723(1)	
32	Ge	Germanium	72.64(1)	
79	Au	Gold	196.966569(4)	
72	Hf	Hafnium	178.49(2)	
108	Hs	Hassium	[270]	5
2	He	Helium	4.002602(2)	1, 2
67	Ho	Holmium	164.93032(2)	
1	H	Hydrogen	1.00794(7)	1, 2, 3
49	In	Indium	114.818(3)	
53	I	Iodine	126.90447(3)	
77	Ir	Iridium	192.217(3)	
26	Fe	Iron	55.845(2)	
36	Kr	Krypton	83.798(2)	1, 3
57	La	Lanthanum	138.90547(7)	1
103	Lr	Lawrencium	[262]	5
82	Pb	Lead	207.2(1)	1, 2
3	Li	Lithium	6.941(2)	1, 2, 3, 4
71	Lu	Lutetium	174.9668(1)	1
12	Mg	Magnesium	24.3050(6)	
25	Mn	Manganese	54.938045(5)	
109	Mt	Meitnerium	[276]	5
101	Md	Mendelevium	[258]	5
80	Hg	Mercury	200.59(2)	
42	Mo	Molybdenum	95.96(2)	1
60	Nd	Neodymium	144.242(3)	1
10	Ne	Neon	20.1797(6)	1, 3
93	Np	Neptunium	[237]	5
28	Ni	Nickel	58.6934(4)	
41	Nb	Niobium	92.90638(2)	
7	N	Nitrogen	14.0067(2)	1, 2
102	No	Nobelium	[259]	5
76	Os	Osmium	190.23(3)	1
8	O	Oxygen	15.9994(3)	1, 2
46	Pd	Palladium	106.42(1)	1
15	P	Phosphorus	30.973762(2)	
78	Pt	Platinum	195.084(9)	
94	Pu	Plutonium	[244]	5
84	Po	Polonium	[209]	5
19	K	Potassium	39.0983(1)	1
59	Pr	Praseodymium	140.90765(2)	
61	Pm	Promethium	[145]	5
91	Pa	Protactinium	231.03588(2)	5
88	Ra	Radium	[226]	5
86	Rn	Radon	[222]	5
75	Re	Rhenium	186.207(1)	
45	Rh	Rhodium	102.90550(2)	
111	Rg	Roentgenium	[280]	5
37	Rb	Rubidium	85.4678(3)	1
44	Ru	Ruthenium	101.07(2)	1
104	Rf	Rutherfordium	[265]	5
62	Sm	Samarium	150.36(2)	1
21	Sc	Scandium	44.955912(6)	
106	Sg	Seaborgium	[271]	5
34	Se	Selenium	78.96(3)	
14	Si	Silicon	28.0855(3)	2
47	Ag	Silver	107.8682(2)	1
11	Na	Sodium	22.98976928(2)	
38	Sr	Strontium	87.62(1)	1, 2
16	S	Sulfur	32.065(5)	1, 2
73	Ta	Tantalum	180.94788(2)	
43	Tc	Technetium	[98]	5
52	Te	Tellurium	127.60(3)	1
65	Tb	Terbium	158.92535(2)	
81	Tl	Thallium	204.3833(2)	
90	Th	Thorium	232.03806(2)	1, 5
69	Tm	Thulium	168.93421(2)	
50	Sn	Tin	118.710(7)	1
22	Ti	Titanium	47.867(1)	
74	W	Tungsten	183.84(1)	
116	Uuh	Ununhexium	[293]	5
118	Uuo	Ununoctium	[294]	5
117	Uus	Ununseptium	[294]	5
115	Uup	Ununpentium	[288]	5
114	Uuq	Ununquadium	[289]	5
113	Uut	Ununtrium	[284]	5
92	U	Uranium	238.02891(3)	1, 3, 5
23	V	Vanadium	50.9415(1)	
54	Xe	Xenon	131.293(6)	1, 3
70	Yb	Ytterbium	173.054(5)	1
39	Y	Yttrium	88.90585(2)	
30	Zn	Zinc	65.38(2)	
40	Zr	Zirconium	91.224(2)	1

1. Geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic mass of the element in such specimens and that given in the Table may exceed the stated uncertainty.

2. Range in isotopic composition of normal terrestrial material prevents a more precise value being given; the tabulated value should be applicable to any normal material.

3. Modified isotopic compositions may be found in commercially available material because it has been subject to an undisclosed or inadvertant isotopic fractionation. Substantial deviations in atomic mass of the element from that given in the Table can occur.

4. Commercially available Li materials have atomic masses that range between 6.939 and 6.996; if a more accurate value is required, it must be determined for the specific material [range quoted for 1995 tables 6.94 and 6.99].

5. Element has no stable nuclides. The value enclosed in brackets, e.g. [209], indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic mass is tabulated.

The names and symbols for elements 113–118 are under review. The temporary system recommended by J Chatt, *Pure Appl. Chem.*, **51**, 381–384 (1979) is used above.

RELATIONSHIPS AMONG UNITS

(Values in boldface are exact.)

Length

1 in. = **2.54** cm
1 ft = **30.48** cm
1 yd = **0.9144** m
1 mi = **5280** ft
1 ft = **12** in.
1 yd = **36** in.

Volume

1 liq. oz = **29.57353** mL
1 qt = **946.352946** mL
1 gallon = **3.785411784** L
1 gallon = **4** qt = **8** pt
1 qt = **2** pt = **32** liq. oz

Mass

1 oz = **28.349523125** g
1 lb = **453.59237** g
1 lb = **16** oz

Pressure

1 atm = **760** torr
1 atm = **101,325** Pa
1 atm = 14.696 psi (lb/in.^{2})
1 atm = 29.921 in. Hg

Energy

1 cal = **4.184** J
1 ev = 1.6022 × 10^{-19} J
1 ev/molecule = 96.49 kJ/mol
1 ev/molecule = 23.06 kcal/mol
1 J = 1 kg m^2 s^{-2} = 10^7 erg

PHYSICAL CONSTANTS

Rest mass of electron	$m_e = 5.485799094 \times 10^{-4}$ u ($9.1093821 \times 10^{-28}$ g)
Rest mass of proton	$m_p = 1.0072764668$ u ($1.67262164 \times 10^{-24}$ g)
Rest mass of neutron	$m_n = 1.0086649160$ u ($1.67492721 \times 10^{-24}$ g)
Electronic charge	$e = 1.60217649 \times 10^{-19}$ C
Atomic mass unit	$u = 1.66053878 \times 10^{-24}$ g
Gas constant	$R = 0.0820575$ L atm mol^{-1} K^{-1} $= 8.31447$ J mol^{-1} K^{-1} $= 1.98721$ cal mol^{-1} K^{-1}
Molar volume, ideal gas	= 22.4140 L (at STP)
Avogadro's number	$= 6.0221418 \times 10^{23}$ things/mol
Speed of light in a vacuum	$c = 2.99792458 \times 10^8$ m s^{-1} (Exactly)
Planck's constant	$h = 6.6260690 \times 10^{-34}$ J s
Faraday constant	$F = 9.6485340 \times 10^4$ C mol^{-1}

LABORATORY REAGENTS

(Values are for the average concentrated reagents available commercially.)

	Percent	Mole Solute	Gram Solute
Reagent	(w/w)	Liter Solution	100 mL Solution
NH_3	29	15	26
$HC_2H_3O_2$	99.7	17	105
HCl	37	12	44
HNO_3	71	16	101
H_3PO_4	85	15	144
H_2SO_4	96	18	177

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PERIODIC TRENDS

(Trends in the following properties that can be correlated with the periodic table are discussed in the given sections.)

Metallic versus nonmetallic properties	3.3
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